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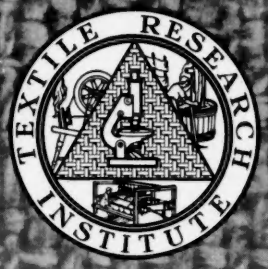

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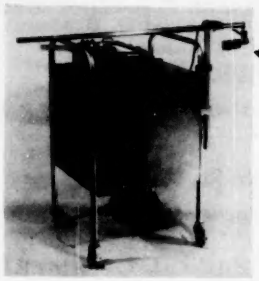

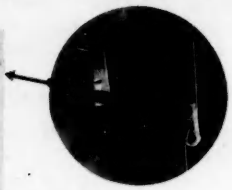

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TEXTILE RESEARCH JOURNAL

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Studies of the Dyeing of Nylon with Acid Dyes

Part II: Kinetics of the Process

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Abstract

The rate of uptake by nylon of nine acid dyes and 21 binary mixtures thereof have been determined at pH 3 and 75° C. using infinite dye bath conditions. The results have been analyzed by a modified diffusion equation in which the flux of dye is assumed proportional to the gradient of activity of the dye on the fiber. This equation enables the adsorption of two dyes to be treated and leads to the result that the uptake of dye 1 is proportional to that of dye 2, a fact which is confirmed by the experimental data. The slope of a graph of the uptake of dye 1 versus dye 2 is related to the ratio of the diffusion coefficients, the affinities of the dyes for the fiber, and the concentrations of the dyes in the bath. Using diffusion coefficients deduced from the rate of uptake of the dyes taken singly, the affinity difference of each binary pair has been calculated. The results obtained are discussed with reference to affinity data on the same dyes obtained by desorption techniques.

To obtain a complete insight into the adsorption of dyes by fibers, attention must be devoted to the kinetics of the process as well as to the equilibria attained. The classical work of Neale, *et al.*, has shown that, to a first approximation, the kinetics can be described in terms of the laws of diffusion. Garvie and Neale [7] investigated the diffusion of a direct cotton dye, Chlorazol Sky Blue FF, into "Cellophane" by following the uptake of dye by several sheets of this material, held in the form of a multilayered sandwich, as a function of time. These experiments enabled concentration/penetration profiles to be constructed for different times of dyeing, and since they provided complete information on the distribution of dye within the substrate, this work represents the most fundamental body of data yet obtained on the diffusion of dyes. Using this data, multiple estimates of the diffusion coefficient were made by graphical methods, using Fick's first law,

$$S = -D(\partial c/\partial x) \qquad (1)$$

where S is the amount of dye passing through unit area in unit time, D is the diffusion coefficient, and c is the concentration of dye at the point x in the slab. Equation 1 states that the rate of diffusion is proportional to the concentration gradient and that the diffusion coefficient is a true constant, and

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is known to be obeyed accurately by diffusion processes in the gaseous phase. It is also well known that in more condensed systems this simple law is not obeyed, in that the diffusion coefficient as measured is found to be an increasing function of the concentration of the diffusing species. In the particular case of the diffusion of dyes, the causes of nonideal behavior are not difficult to find, the most important one being that diffusion and adsorption of the dye occur simultaneously. Additional complications arise from the existence of barriers of electrical potential at the fiber-water interface, the magnitude of which will vary with electrolyte concentration.

In view of these complications it is not surprising that the curves of dye penetration obtained by Garvie and Neale [7] were not of the same shape as would have been derived from Fick's Law, nor that the values of the diffusion coefficient varied markedly with concentration, according to the equation

$$D_m = Dc^{0.5} \tag{2}$$

where D_m is the measured diffusion coefficient, D is a constant, and c is the concentration of dye. The experimental data was later reexamined by Crank [5], who derived the relation

$$D_m = D(1 + 0.25c) \tag{3}$$

as being a better mathematical representation of the data than Equation 2. Although the approach to the problem adopted by Neale is the most rigorous which could be envisaged, it requires an enormous amount of experimental work in order to characterize a single dye and cannot be adopted in studies of the properties of a number of dyes. A method which is less fundamental, although much simpler experimentally, is to deduce the diffusion coefficient from a "rate of dyeing" graph. In this method the uptake of dye by the fiber from an infinite dye bath is plotted as a function of time, and the diffusion coefficient is derived by fitting a curve representing the solution of Fick's second law, relevant to the geometric nature of the system (e.g., planar, cylindrical).

$$\left(\frac{\partial c}{\partial t}\right) = D\nabla^2 c \tag{4}$$

Solutions of this equation can readily be obtained for different systems if the boundary condition of constant dye concentration at the dyeing surface is employed. This concentration is the same as that adsorbed by the substrate at equilibrium, i.e., C_∞ and leads to the following equation for a thin, semi-infinite slab of thickness b,

$$C(t, x) = C_\infty \cdot f(D, t, x/b^2) \tag{5}$$

where $C(t, x)$ is the concentration at a point x within the medium at time t. Equation 5 can be integrated to give the total quantity of dye which the material adsorbs, as a function of time.

$$Q_t = Q_\infty \left[1 - \frac{8}{\pi^2}\left(e^{-\pi^2 Dt/b^2} + \frac{1}{9}e^{-9\pi^2 Dt/b^2} + \frac{1}{25}e^{-25\pi^2 Dt/b^2} \ldots\right)\right]$$

where Q_t is the amount of dye adsorbed at time t, and Q_∞ that at infinite time (i.e., at equilibrium). A similar equation has been derived by Hill [9] when the system is cylindrical and this is the solution normally applied to fibers. The assumption of constant concentration at the dyeing surface tacitly implies that on immersion of the fiber into the dye liquor, a layer of dye of concentration C_∞ is immediately formed at the outside surface and that diffusion of dye proceeds from this layer into the substrate.

By using such solutions of Fick's equation, Neale and Stringfellow [11] determined the diffusion coefficients of a number of direct dyes and showed that where data were available for comparison, the results of this method were in agreement with those deduced from concentration profiles, by the methods previously described. The method based on the rate of dyeing curve obviously gives an average value for D, since at any time during the dyeing, a range of concentrations is present in the fiber. With this technique, much information has been accumulated on the variation of D with dye bath conditions, but the interpretation of the results is not easy because of uncertainty as to the exact nature of the average concentration of dye in the fiber.

Attempts have therefore been made to refine the analysis by the use of a more detailed physical model to represent the substrate. Standing and others [12] have regarded the substrate as being heterogeneous, by making allowance for the water within the fiber. This internal aqueous phase was assumed to be in the form of a series of canals or pores down which the dye diffused. It was also assumed that the equilibrium was maintained at all

points in the fiber between the dye adsorbed on the pore walls and that in the internal aqueous phase. Analysis of this model gave a modified form of the diffusion equation, in which the diffusion coefficient was replaced by $D_0/(1 + R)$, where D_0 is the free diffusion coefficient of the dye in solution and R is the ratio of the concentrations of dye on the pore wall and in solution, being determined by the adsorption isotherm. This equation makes the measured diffusion coefficient a function of dye concentration.

Crank [4], on the other hand, has modified the diffusion equations to take account of the electrical repulsions which occur between the dye anions and the negatively charged fiber, and his treatment introduced a dependence of D on electrolyte concentration. By such approaches these authors have indicated the probable causes of the experimentally observed variations of D, but the amount of work carried out to date can at best be considered only a partial solution to the problem.

Taking for granted the dependence of D on c, Crank and Henry [6] have more recently shown that solutions of the equation

$$S = \frac{-\partial(D, c)}{\partial x} \tag{6}$$

in which D is regarded as a function of concentration, lead to concentration profiles more in accord with those observed experimentally. For many practical purposes, however, the range of values of the diffusion coefficient for a group of dyes (such as the direct cotton class) is so large that the diffusion coefficients serve as useful parameters for characterizing the dyeing properties. Thus the present position is that the deficiencies of Fick's law as a quantitative explanation of the diffusion of dyes in fibrous substrates are well known, and several investigations have shown how D varies with c. There is as yet no general treatment of diffusion able to yield a diffusion coefficient or other parameter which would enable dyeing behavior to be calculated under all conditions. In general studies of dyeing kinetics, therefore, it has been necessary to assume the validity of Fick's law and to interpret the results with caution because of the possible variations of D with c.

To date, little information has been published on the kinetics of the uptake of acid dyes by nylon and, in particular, the uptake from infinite dye baths, studies of which are the most convenient for the calculation of diffusion coefficients. The concept of dyeing as a diffusion controlled process has, however, been used to explain the observed differences between the uptake rates of mono-, di-, and trisulphonated dyes, and the incompatibility of acid dyes in mixtures on nylon. The latter aspect is deserving of attention since it is the greatest source of technical difficulty in the dyeing of nylon, but to date no data have been available which refer to experimental conditions capable of theoretical interpretation. Thus, while the data of Abbott, Crook, and Townend [1] on the rate of dye bath exhaustion from mixtures of Tartrazine N and Lissamine Red 7BP are instructive in illustrating the extent to which incompatibility can occur under practical conditions, they do not form a basis for a theoretical investigation.

The factors operative in the dyeing of nylon from mixed dye baths have been discussed by Meggy [10] and a method proposed for assessing compatibility in terms of fundamental quantities. He considers a dye bath containing an equimolar mixture of two dyes (1 and 2) and a fiber divided macroscopically into two separate portions which are occupied by the two dyes. The relative areas of fiber available are assumed to depend on the relative affinities of the dyes

$$\frac{a_1}{a_2} = \frac{e^{-\Delta\mu_1^0/RT}}{e^{-\Delta\mu_2^0/RT}} \tag{7}$$

where a_1 and a_2 represent the fraction of the fiber surface area covered by dyes 1 and 2, and $\Delta\mu_1^0$ and $\Delta\mu_2^0$ are the affinities of the two dyes. If the rates of diffusion of the two dyes per unit area are r_1 and r_2, respectively, then the rates of adsorption will be $a_1 \cdot r_1$ and $a_2 \cdot r_2$. It is then assumed that r_1 and r_2 may be replaced by the respective diffusion coefficients and hence the relative rates of adsorption are

$$\frac{a_1 D_1}{a_2 D_2} = \frac{e^{-\Delta\mu_1^0/RT}}{e^{-\Delta\mu_2^0/RT}} \times \frac{D_1}{D_2} \tag{8}$$

This gives the factor $De^{-\Delta\mu^0/RT}$ as the quantity determining the compatibility of the dyes when used in admixture. There is some indication that this factor is of practical value in discussing compatibility, although this derivation contains some obvious fallacies in terms of the model used. Thus the division of the surface macroscopically implies that each dye diffuses down its own concentration gradient independently; that is to say, although competition is assumed at the surface of the fiber

no such interaction is considered inside it. The rate of dyeing curves obtained when two dyes are used in admixture should therefore be regular in shape and have the same time of half-dyeing as when the dyes were used singly. There is no experimental evidence available on the last point, but in view of the large degrees of incompatibility observed in practice, it is unlikely to be true for nylon. Again if Fick's law is obeyed, there is no reason for replacement of the rate of uptake by the diffusion coefficient. This is shown by writing the relative rates of uptake in terms of Fick's law.

$$\frac{a_1 r_1}{a_2 r_2} = \frac{a_1}{a_2} \times \frac{D_1}{D_2} \times \frac{(\partial c_1/\partial x)}{(\partial c_2/\partial x)} \qquad (9)$$

It is apparent from this equation that the use of the diffusion coefficient rather than the uptake rate is justified only if the ratio of the concentration gradients is time independent. No discussion of this point is given by Meggy.

It is possible to investigate the model used by Meggy, rather more accurately on the basis of Hill's equation. With the assumption of macroscopic division of the fiber, the relative uptake rates may be calculated throughout the dyeing process. It is assumed that the dye bath is infinite so that no changes in either total concentration or composition occur. (It should be pointed out that this assumption is tacitly made by Meggy, and therefore his conclusions, if applied to practical dyeing in which dye bath exhaustion occurs, can be true only for the early stages of dyeing.) These assumptions lead to the equations

$$Q_1 = Q_{1\infty}[1 - 0.692\ (e^{-5.785\,D_1 t/r^2} + 0.190\,e^{-30.5\,D_1 t/r^2} + 0.0775\,e^{-74.9\,D_1 t/r^2} \cdots)] \qquad (10)$$

and

$$Q_2 = Q_{2\infty}[1 - 0.692\ (e^{-5.785\,D_2 t/r^2} + 0.190\,e^{-30.5\,D_2 t/r^2} + 0.0775\,e^{-74.9\,D_2 t/r^2} \cdots)]$$

where Q_1 and Q_2 are the amounts of dye taken up at time t and $Q_{1\infty}$, and $Q_{2\infty}$ are the amounts of dye taken up at infinite time (corresponding to Meggy's a_1 and a_2 terms). D_1 and D_2 are the diffusion coefficients. The ratio of the two dyes taken up is a function of time as may be shown by plotting $Q_2/Q_{2\infty}$ against $Q_1/Q_{1\infty}$ (Figure 1). The nonconstancy of the uptake ratio is clearly evident when the fiber has dyed to about 50 to 60% of its final value. The deviation from linearity depends on the values of the diffusion coefficients, being least for small values of $(D_1 - D_2)$ and time. With this proviso, the ratio reduces to the form given by Meggy, i.e.,

$$\frac{Q_{1\infty}}{Q_{2\infty}} \times \frac{D_1}{D_2}$$

It is apparent, however, that so long as Fick's law is assumed, no further simplification of the problem can be effected.

The fundamental difficulty stems from the inability of Fick's law to represent diffusion in a medium for which there is a limit to the total amount of dye which can be accommodated, as for instance in the case of nylon. The diffusion of dyes in this fiber must be governed not only by the concentration gradient of the dye but also by the ability of the fiber to accept further quantities of dye (to which there is a limit under normal dyeing conditions, governed by the amino-group content of the fiber).

It is more logical in these circumstances to assume that the driving force of diffusion is some function of the fraction of dyeing sites occupied by the dye θ and also those unoccupied $(1 - \theta)$. By analogy with the thermodynamic treatment of dye adsorption given in a previous paper [2], the most appropriate quantity would seem to be the ratio of these two quantities, i.e., $\theta/(1 - \theta)$. This quantity is the activity (for a monobasic dye) and its replacement of the concentration is in keeping with the normal concepts of physical chemistry. The replacement of concentration by activity in diffusion equations has in fact already been suggested by Barrer [3] as being a possible method of circum-

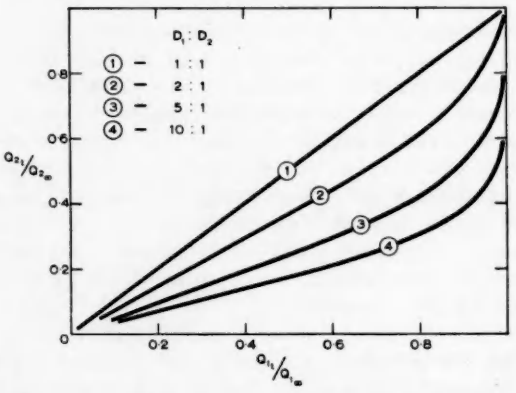

Fig. 1. Hypothetical curves derived from Hill's equation.

venting the complexities which arise from the breakdown of Fick's equation. On this basis therefore the fundamental law of diffusion for a dye of basicity z would be

$$S = -D\left(\frac{\partial a}{\partial x}\right) = -\frac{D}{z}\frac{\partial}{\partial x}\left[\frac{\theta}{1-\theta}\right] \quad (11)$$

where a is the activity given by

$$\frac{1}{z}\left(\frac{\theta}{1-\theta}\right),$$

and S is the diffusion per unit area of fiber.

Concentration could be replaced by the chemical potential μ of the species at any point, as has been suggested by Hartley [8]. The equation in this case becomes

$$S = -D\theta\frac{\partial\mu}{\partial x} = -D\theta\frac{\partial(\log a)}{\partial x}$$

and leads to the same final result for mixtures of dyes as the simpler Equation 11. Equation 11 represents a departure from the customary method of treating nonideal diffusion behavior, which is to assume that the concentration gradient is the driving influence and that breakdowns are due to variation of the diffusion coefficient. Differentiation of Equation 10 with respect to x shows that the apparent diffusion coefficient will in fact be an increasing function of dye concentration, thus

$$S = \frac{-D}{z(1-\theta)^2}\left(\frac{\partial\theta}{\partial x}\right) \quad (12)$$

This is equivalent to Fick's first law, with the diffusion coefficient given by $D/[z(1-\theta)^2]$. It follows from this that if a diffusion coefficient is calculated on the basis of Fick's law, it will involve the basicity of the dye as well as some kind of average concentration. In order to calculate D from Equation 12, it would be necessary to measure $(\partial\theta/\partial x)$ and θ as well as S. This could be done only by a technique similar to that used by Garvie and Neale [7], involving the measurement of concentration/distance curves within the fiber. Unfortunately, nylon is not readily available in sheet form, and fabrication of samples to the requisite standard of homogeneity and reproducibility for measurements of the kind envisaged would be a formidable undertaking. At the present time, therefore, considerable difficulty attaches to the direct evaluation of Equation 12.

The alternative course of determining D from measurements of uptake rate necessitates the derivation of a second equation analogous to Fick's second law. The relevant equation in the present case is

$$\left(\frac{\partial n}{\partial t}\right) = p\left(\frac{\partial\theta}{\partial t}\right) = \frac{\partial}{\partial x}\left\{\left[\frac{D}{z(1-\theta)^2}\right]\cdot\frac{\partial\theta}{\partial x}\right\} \quad (13)$$

where p is the total number of dyeing sites and n the number of dye molecules per unit mass of fiber. When the right-hand side is differentiated, the following equation is obtained.

$$\left(\frac{\partial\theta}{\partial t}\right) = \frac{D}{p\cdot z}\left[\frac{1}{(1-\theta)^2}\cdot\frac{\partial^2\theta}{\partial x^2} + \frac{2}{(1-\theta)^3}\cdot\left(\frac{\partial\theta}{\partial x}\right)^2\right] \quad (14)$$

which is to be compared with Fick's equation

$$\left(\frac{\partial\theta}{\partial t}\right) = D\left(\frac{\partial^2\theta}{\partial x^2}\right)$$

It is clear from the complicated form of the right-hand side of Equation 14 that it is impossible to determine D from simple experiments on uptake rate. Thus the present position is that, because of the type of experimental work which could be undertaken in these studies (which were primarily aimed at comparison of the dyeing properties of different dyes, rather than a complete solution of the diffusion equation for one particular dye), it was not possible to measure and use values of the true diffusion coefficient, as indicated by Equations 12 and 14. Instead it was necessary to use the customary procedure of applying Fick's law to data on the rate of uptake of dyes. In order to minimize errors arising from this procedure, the dyeings were carried out at concentrations similar to those used subsequently in experiments involving mixtures of dyes. Equations 12 and 14 indicate that the values of the diffusion coefficient so obtained will be modified by the basicity of the dye and saturation value of the fiber. In order to avoid confusion, therefore, the symbol F will be used subsequently to denote the diffusion coefficient obtained by the application of Fick's law to measurements of uptake rate.

Equation 11 is particularly suitable for the analysis of the simultaneous uptake of two dyes, since it allows for the effect of the presence of one dye on the diffusion flux of the other. Thus for the simultaneous diffusion of two dyes into the fiber, two

equations may be written

$$S_1 = \frac{dQ_1}{dt} = - F_1 \cdot \frac{\partial}{\partial x}\left(\frac{\theta_1}{1 - \theta_1 - \theta_2}\right)$$

and (15)

$$S_2 = \frac{dQ_2}{dt} = - F_2 \cdot \frac{\partial}{\partial x}\left(\frac{\theta_2}{1 - \theta_1 - \theta_2}\right)$$

in which S_1 and S_2 are the fluxes of dyes 1 and 2. Since both θ_1 and θ_2 are functions of x, these equations may be differentiated to give

$$\frac{dQ_1}{dt} = - F_1 \cdot \left[\frac{(1 - \theta_2)\left(\frac{\partial \theta_1}{\partial x}\right) + \theta_1\left(\frac{\partial \theta_2}{\partial x}\right)}{(1 - \theta_1 - \theta_2)^2}\right]$$

and (16)

$$\frac{dQ_2}{dt} = - F_2 \cdot \left[\frac{(1 - \theta_1)\left(\frac{\partial \theta_2}{\partial x}\right) + \theta_2\left(\frac{\partial \theta_1}{\partial x}\right)}{(1 - \theta_1 - \theta_2)^2}\right]$$

So far the theory refers to any point within the fiber at distance x from the dyeing surface. Under the dyeing conditions used in the present work, where the dye bath is infinite, the surface concentration, once established, will remain constant throughout the dyeing, both in magnitude and composition with respect to the dyes. If Equations 16 above are applied to the outer surface of the fiber, then dQ_1/dt and dQ_2/dt become the rates of change of the total amounts of the two dyes on the fiber.

Under these conditions, however, the equations are difficult to manipulate, since because of the high affinity of acid dyes for nylon, the outside surface of the fiber will in general be almost saturated with dye, and the function $(1 - \theta_1 - \theta_2)$ will be very small. This term can, however, be eliminated if Equations 16 are divided.

$$\frac{dQ_1}{dt} \Big/ \frac{dQ_2}{dt} = \frac{F_1}{F_2}\left[\frac{(1 - \theta_2)\left(\frac{\partial \theta_1}{\partial x}\right) + \theta_1\left(\frac{\partial \theta_2}{\partial x}\right)}{(1 - \theta_1)\left(\frac{\partial \theta_2}{\partial x}\right) + \theta_2\left(\frac{\partial \theta_1}{\partial x}\right)}\right] = \frac{F_1\theta_1}{F_2\theta_2}\left[\frac{\left(\frac{1 - \theta_2}{\theta_1}\right)\left(\frac{\partial \theta_1}{\partial x}\right) + \left(\frac{\partial \theta_2}{\partial x}\right)}{\left(\frac{1 - \theta_1}{\theta_2}\right)\left(\frac{\partial \theta_2}{\partial x}\right) + \left(\frac{\partial \theta_1}{\partial x}\right)}\right] \quad (17)$$

However, for high degrees of surface saturation $(1 - \theta_1) \sim \theta_2$ and $(1 - \theta_2) \sim \theta_1$, and if these approximations are applied, Equation 17 reduces to the simple expression

$$\frac{(dQ_1/dt)}{(dQ_2/dt)} = \frac{F_1\theta_1}{F_2\theta_2} \quad (18)$$

which indicates that the ratio of the relative dyeing rates will be time independent so long as the surface concentrations do not change. If in addition the affinity difference of the dyes is known, the relation between the dye concentrations in the fiber and in solution is established, and Equation 18 may be written

$$\frac{dQ_1}{dt} \Big/ \frac{dQ_2}{dt} = \frac{F_1 z_1 C_{B1}}{F_2 z_2 C_{B2}} \cdot e^{-(\Delta\mu_1^0 - \Delta\mu_2^0)/RT} \quad (19)$$

where $\Delta\mu_1^0$ and $\Delta\mu_2^0$ are the affinities of the dyes and C_{B1} and C_{B2} are the concentrations of the dyes in solution.

Thus the uptake of binary mixtures of acid dyes by nylon from infinite dye baths is controlled by the affinities, diffusion coefficients, basicities, and concentrations of dyes in the dye bath. The equation is similar to that obtained by Meggy, but the basis for its validity is now the assumption that the driving force is the gradient of activity of the dye in the fiber. This equation cannot at the moment be checked, owing to the lack of suitable experimental data in the literature. The work described subsequently was undertaken in order to provide such data, the dyeings having been made from infinite dye baths using a series of acid dyes, singly and in binary mixtures.

Experimental

In order to test the theory of uptake from mixtures of dyes, rate of dyeing curves were prepared singly for 9 acid dyes and for 21 different binary combinations thereof. The details were as follows.

i. *Materials.* 15-den. microdull nylon monofil, which had been shown by hydrochloric acid titration of a phenol/methanol solution to have a free amino group content of 35 meq./kg., was used throughout. It was wound into hanks of about 0.3 g. each which were scoured in Lissapol N and soda ash solution at 80° C. for 30 min. and washed thoroughly in distilled water for 18 hr. The hanks were dried at 70° C. before use.

Commercial dyes were used after their pure dye content had been estimated by colorimetric comparison with purified material. The technique of purification has been described in an early paper [2].

ii. *Method of dyeing.* The dye baths were prepared containing 1 g./liter of each component to a total volume of 2 liters. To each was added 3 ml./liter of 20% formic acid solution, and the initial dye bath pH was measured. The values varied between 2.8 and 3.0.

The dye bath temperature was raised to 75° C. in a thermostatic water bath with stirring. The rate of agitation was so chosen that further increase thereof produced no corresponding increase in the rate of dye uptake by the fiber. Twelve hanks of 0.3 g. each were immersed in the dye bath and removed in pairs after periods of 2, 5, 10, 20, 40, and 60 min., rinsed immediately in cold distilled water, and dried at 70° C. (In some of the experiments, it proved necessary to increase the dyeing times to 5, 15, 30, 60, 120, and 300 min.; otherwise an identical technique was adopted throughout.)

iii. *Estimation of dye adsorbed by fiber.* After drying, the hanks were cooled in a desiccator, and the dye content of the fiber was estimated by dissolution of a weighed amount in ortho chlorophenol which would give a solution having an optical density suitable for measurement in a 1-cm. optical cell. The absorption spectra of the solutions were measured between 400 and 750 mμ using a Cary recording spectrophotometer.

Because of the delustrant contained in the fiber, the solutions were faintly opalescent, and it was necessary to correct the measured optical densities for this scattering of light. When ortho chlorophenol solutions of scoured, undyed nylon were prepared at a range of fiber concentrations, measurement of their absorption spectra indicated that over the small concentration range applicable, the optical density at any single wave length within the visible spectrum was proportional to the optical density at 750 mμ, a wave length at which the dyes were nonabsorbing.

Having measured the optical density of the solution of the fiber at the wave lengths of maximum absorption of the two components of the mixture and corrected for the delustrant contribution, the concentration of each component in the fiber was obtained by solving two simultaneous equations.

$$D_{\lambda_1} = A_{\lambda_1} \cdot C_1 + B_{\lambda_1} \cdot C_2$$
$$D_{\lambda_2} = A_{\lambda_2} \cdot C_1 + B_{\lambda_2} \cdot C_2$$

where

C_1 and C_2 are the concentrations of dyes 1 and 2 in the solution of the fiber.

D_{λ_1} and D_{λ_2} are the corrected optical densities of the dye solution at λ_1 and λ_2, the wave lengths of maximum absorption of dyes 1 and 2.

A_{λ_1} and A_{λ_2} are the densities of a solution of dye 1 at unit concentration at λ_1 and λ_2, and

B_{λ_1} and B_{λ_2} are the corresponding values for dye 2.

iv. *Estimation of equilibrium values for calculation of F/ρ^2.* It was apparent from the rate of uptake curves obtained for single dyes that a dyeing time of 300 min. was inadequate for the establishment of equilibrium with the majority of the dyes used. Under the conditions of dye concentration, pH, and temperature used previously, a loose plug of staple fiber obtained from the continuous filament used throughout was dyed for 24 hr. in a closed tube at an infinitely long liquor length. The dye uptake was again determined by colorimetric estimation of an ortho chlorophenol solution.

It was found that further increase in dyeing time had no measurable effect on the amount of dye adsorbed.

Results and Discussion

The uptake rate curves of 9 dyes in binary mixtures (21 in all) were determined from dye baths of pH 3.2, containing 1 g. of dye per liter. Typical curves are shown in Figures 2 and 3, in which the amount of each dye absorbed, in millimoles/kg. of fiber, is plotted against time. The curves are of the same general shape as those found for the uptake of a single dye, rising rapidly in the early stages of dyeing and approaching steady values as time proceeds.

The most direct way of checking Equation 19 would be to determine values of dQ_1/dt and dQ_2/dt graphically, by drawing tangents to the uptake/time curves. This process, however, is subject to the objection that excessive experimental errors may arise due to imperfections of technique.

An equally significant but more precise check upon the theory is afforded by integrating Equation 19 to give

$$Q_1 = \left[\frac{F_1}{F_2} \cdot \frac{C_{B_1}}{C_{B_2}} \cdot \frac{z_1}{z_2} \cdot e^{-(\Delta\mu_1^0 - \Delta\mu_2^0)/RT} \right] Q_2 + K \quad (20)$$

This indicates that a plot of Q_1 against Q_2 should be linear, with a gradient of

$$\frac{F_1}{F_2} \cdot \frac{C_{B_1}}{C_{B_2}} \cdot \frac{z_1}{z_2} \cdot e^{-(\Delta\mu_1^0 - \Delta\mu_2^0)/RT}$$

and an intercept of K on the Q_1 axis. The linearity of such a plot is therefore a good test of Equation 19. The significance of K is more doubtful. If it is assumed that the layer of dye, which is adsorbed onto the outer surface of the fiber immediately upon immersion in the dye bath, has exactly the same composition as the mixtures of dyes which would be on the fiber in equilibrium with the same dye bath, then Q_1 and Q_2 should simultaneously approach zero as $t \rightarrow 0$, in such a way that K will be zero. Stated differently, this means that at all times, even within the period immediately after immersion, when the surface layer is being established, the relative rates of uptake will be in the same ratio as those which occur a short time later, when the outer surface is effectively in equilibrium with the dye bath and dye uptake is proceeding by diffusion within the fiber. This argument is not, however, likely to be correct, since it ignores factors such as differences in the free diffusion coefficients in solution of the dyes which, although not material to considerations of diffusion within the fiber, will affect the rate at which the adsorbed layer of dye on the outer surface of the fiber is established. Thus it is to be expected that in general K will have a finite value, and this is confirmed by the experimental data. The point of significance for the present discussion, however, is the linearity of the Q_1/Q_2 plots. In every mixture investigated, it was possible to obtain a good fit to a straight line, typical results being shown in Figures 4 and 5. The gradients of the plots for all the mixtures investigated are shown in Table I, the detailed results being given in the Appendix.

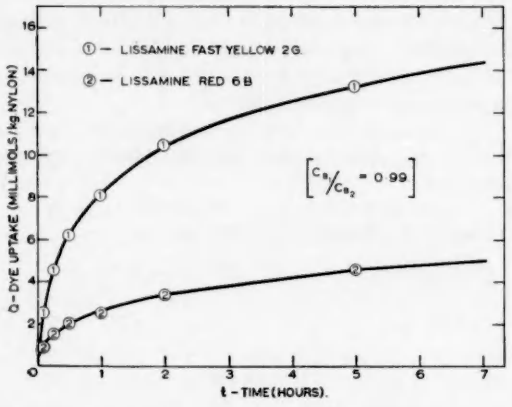

Fig. 2. Rate of dyeing curves from infinite dye bath at 75° C. for binary mixture of Lissamine Fast Yellow 2G and Lissamine Red 6B.

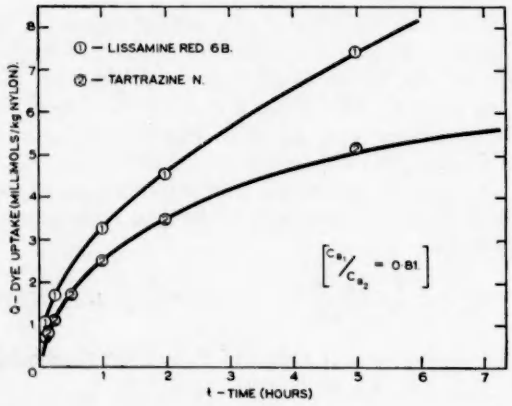

Fig. 3. Rate of dyeing curves from infinite dye bath at 75° C. for binary mixture of Lissamine Red 6B and Tartrazine N.

Notwithstanding the fact that values of

$$\frac{F_1}{F_2} \cdot \frac{C_{B_1}}{C_{B_2}} \cdot \frac{z_1}{z_2} \cdot e^{-(\Delta\mu_1 - \Delta\mu_2)/RT}$$

were determined in this way from the integral equation (Equation 20), the original notation is preserved in subsequent tables, i.e., $\frac{(dQ_1)}{(dt)} \Big/ \frac{(dQ_2)}{(dt)}$ is used to represent experimentally determined values of dQ_1/dQ_2 (the gradient of the linear plot of Q_1 against Q_2).

Another experimental check on the validity of Equation 19 was secure from dyeings obtained with dye baths containing a given pair of dyes, present in different ratios. Four different dye combinations were studied, the results of two of these being shown in Figure 6 in which the slopes of the Q_1/Q_2 graphs are plotted against C_{B_1}/C_{B_2}.

In each case a good fit to a straight line is again obtained. The detailed results corresponding to these plots are given in the Appendix.

As a final check, the cyclical computation was carried out. Since each dye was applied from a dye bath of 1 g./liter, it was possible to calculate the value of $\frac{dQ_1}{dt} \Big/ \frac{dQ_2}{dt}$ from results obtained using mixtures of dyes 1 and 2, and 2 and 3. Thus Equation 19 could be written

$$\frac{dQ_1}{dt} \Big/ \frac{dQ_2}{dt} = \frac{F_1}{F_2} \cdot \frac{C_{B_1}}{C_{B_2}} \cdot \frac{z_1}{z_2} \cdot \frac{e^{-\Delta\mu_1^\circ/RT}}{e^{-\Delta\mu_2^\circ/RT}} = \frac{A_1}{A_2}$$

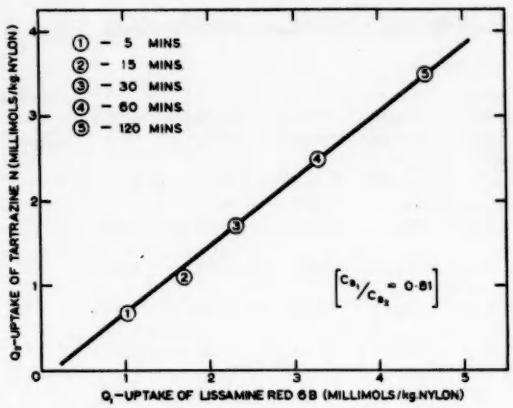
① – 5 MINS
② – 15 MINS
③ – 30 MINS
④ – 60 MINS
⑤ – 120 MINS
$\left[C_{s_1}/C_{s_2} = 0.81\right]$
Q_2–UPTAKE OF TARTRAZINE N (MILLIMOLS/kg NYLON)
Q_1–UPTAKE OF LISSAMINE RED 6B (MILLIMOLS/kg NYLON)

Fig. 4. Relative dye uptake from infinite dye bath at 75° C. from binary mixture of Lissamine Fast Yellow 2G and Lissamine Red 6B.

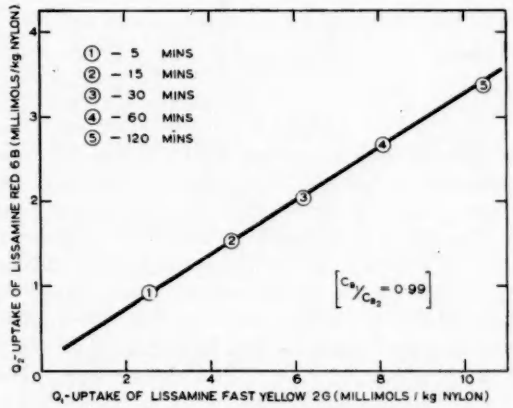
① – 5 MINS
② – 15 MINS
③ – 30 MINS
④ – 60 MINS
⑤ – 120 MINS
$\left[C_{s_1}/C_{s_2} = 0.99\right]$
Q_2–UPTAKE OF LISSAMINE RED 6B (MILLIMOLS/kg NYLON)
Q_1–UPTAKE OF LISSAMINE FAST YELLOW 2G (MILLIMOLS / kg NYLON)

Fig. 5. Relative dye uptake from infinite dye bath at 75° C. from binary mixture of Lissamine Red 6B and Tartrazine N.

where A_1 and A_2 were regarded as parameters for the dyes concerned. Similarly, for dyes 2 and 3 the ratios of the rates could be written as A_2/A_3. It follows then that the ratio $\frac{dQ_1}{dt} \Big/ \frac{dQ_3}{dt}$ could be derived by multiplication of the results for dyes 1 and 2, and 2 and 3. The data obtained in this work were treated in this fashion, and the results are given in Table II.

It can be seen that, in general, the agreement between calculated and measured values is good, implying that the behavior of acid dyes in mixtures can be represented by single terms in assessing competition under infinite dye bath conditions. Thus, all the checks carried out confirmed the correctness of Equation 19 and the inferences upon which it was based. Another feature of interest is that the equation enables the affinity differences between two dyes to be deduced from a knowledge of $\frac{dQ_1}{dt} \Big/ \frac{dQ_2}{dt}$, the dye bath concentrations, and the diffusion coefficients.

Unfortunately, as discussed previously, the determination of the diffusion coefficients presented considerable difficulty. Thus, although the deficiencies of Fick's law were appreciated, it was of necessity used as a basis for the estimates of diffusion coefficient in the present work.

Rate of uptake curves were therefore obtained for each of the dyes used in the binary mixtures and the times of half dyeing determined. The values thus determined were substituted in the relation

$$\frac{F}{\rho^2} = \frac{0.063}{t_{\frac{1}{2}}}$$

which is obtained from Hill's equation, enabling F/ρ^2 to be calculated. (F is the diffusion coefficient, $t_{\frac{1}{2}}$ is the time of half-dyeing, and ρ the diameter of the fiber.) Since comparisons only between dyes involving the ratios of diffusion coefficients were considered, the data was left in the form F/ρ^2, as ρ cancels from Equation 19.

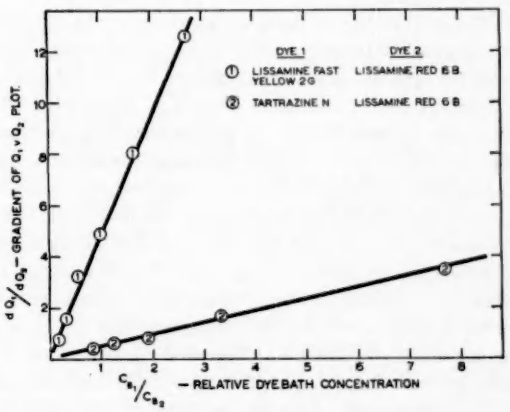
DYE 1
DYE 2
① LISSAMINE FAST YELLOW 2G
LISSAMINE RED 6B
② TARTRAZINE N
LISSAMINE RED 6B
dQ_2/dQ_1 – GRADIENT OF Q_1 v Q_2 PLOT
C_{s_1}/C_{s_2} – RELATIVE DYE BATH CONCENTRATION

Fig. 6. Graph of the gradients of Q_1:Q_2 plots from infinite dye bath at 75° C. from binary mixtures against relative dye bath concentration.

TABLE I. Relative Dyeing Rates, $\frac{dQ_1}{dt} \Big/ \frac{dQ_2}{dt}$, in Binary Mixture of Dyes from Infinite Dye Bath

Dye 1 \ Dye 2	Naphthalene Scarlet 4R (C.I. 185)	Azo Geranine 2G (C.I. 31)	Lissamine Red 6B (C.I. 57)	Lissamine Red 7BP (—)	Lissamine Fast Yellow 2G (C.I. 639)	Tartrazine N (C.I. 640)	Solway Blue A (—)	Solway Blue BN (C.I. 1054)	Naphthalene Fast Orange 2G (C.I. 27)
Naphthalene Scarlet 4R		*	*	*	0.26	3.52	0.71	0.62	*
Azo Geranine 2G	*		*	*	0.53	4.92	0.94	0.83	*
Lissamine Red 6B	*	*		*	0.21	2.43	0.50	0.44	*
Lissamine Red 7BP	*	*	*		1.20	—	1.84	2.77	*
Lissamine Fast Yellow 2G	3.85	1.89	4.75	0.83		*	1.89	1.92	*
Tartrazine N	0.28	0.20	0.41	—	*		0.20	0.18	*
Solway Blue A	1.41	1.06	2.01	0.54	0.53	4.92		*	0.34
Solway Blue BN	1.61	1.21	2.28	0.36	0.52	5.53	*		0.29
Naphthalene Fast Orange 2G	*	*	*	*	*	*	2.94	3.55	

* Optical measurements of these binary mixtures precluded by similarity of absorption spectra.

Dye concentrations of 1 g./liter were employed throughout these experiments. This concentration was chosen to give conditions corresponding as closely as possible to those obtaining during the mixture dyeings, so as to minimize errors arising from variation of diffusion coefficient with concentration.

The values of F/ρ^2 obtained in this way are shown in Table III.

Using the F/ρ^2 values in Table III, the affinity differences between various pairs of dyes were calculated and are shown in column viii of Table IV. A positive sign indicates that the affinity of the first dye in the mixture is numerically higher than that of the second dye by the amount shown. It is possible to arrange the dyes in an order of affinity from this table. Since Solway Blue A has been measured directly against most of the other dyes, it was used as the reference point. These directly measured values of the affinity difference between Solway Blue A and each of the other dyes are shown in column i of Table V. Further estimates of the affinity differences were obtained by combining appropriate pairs of measurements from Table IV. Thus the value of 1.70 kcal. for the difference of affinity between Lissamine Red 7BP and Solway Blue A, listed at the top of column v, Table IV (under heading Lissamine Fast Yellow 2G) was obtained as follows. The affinity difference between Lissamine Red 7BP and Lissamine Fast Yellow 2G is +1.27 kcal. (Table IV, column viii, line 15) and the affinity difference between Lissamine Fast Yellow 2G and Solway Blue A is +0.43 kcal. (Table IV, column viii, line 16). The difference between Lissamine Red 7BP and Solway Blue A is therefore +1.27 + 0.43 = +1.70 kcal. The average affinity differences are shown in column x, Table V, the standard deviations of the values in the table being shown in column xi where these are significant. Although the variation is relatively large (about 0.2 kcal.), the agreement is satisfac-

TABLE III. Diffusion Coefficients of Dyes at 75° C.

Dye	Time of half dyeing (sec.)	$\frac{F}{\rho^2}$ ($\times 10^{+5}$)
Naphthalene Fast Orange 2G	900	7.00
Solway Blue BN	1440	4.38
Solway Blue A	1920	3.28
Azo Geranine 2G	1980	3.18
Lissamine Fast Yellow 2G	2520	2.50
Naphthalene Scarlet 4R	3240	1.94
Tartrazine N	4310	1.43
Lissamine Red 6B	5280	1.19
Lissamine Red 7BP	8100	0.78

TABLE II. Check on Equation 8—Consistency of Relative Rates of Dye Uptake

i Dye combinations	ii* $\frac{dQ_1}{dt} / \frac{dQ_2}{dt}$	iii* $\frac{dQ_2}{dt} / \frac{dQ_3}{dt}$	iv $\frac{dQ_1}{dt} / \frac{dQ_3}{dt}$ (product of ii and iii)	v* $\frac{dQ_1}{dt} / \frac{dQ_3}{dt}$ (measured directly)
1 Naphthalene Scarlet 4R 2 Solway Blue A 3 Lissamine Fast Yellow 2G	0.71	0.53	0.38	0.26
1 Naphthalene Scarlet 4R 2 Solway Blue A 3 Tartrazine N	0.71	4.92	3.49	3.52
1 Naphthalene Scarlet 4R 2 Solway Blue BN 3 Lissamine Fast Yellow 2G	0.62	0.52	0.32	0.26
1 Naphthalene Scarlet 4R 2 Solway Blue BN 3 Tartrazine N	0.62	5.53	3.43	3.52
1 Azo Geranine 2G 2 Solway Blue A 3 Lissamine Fast Yellow 2G	0.94	0.53	0.50	0.53
1 Azo Geranine 2G 2 Solway Blue A 3 Tartrazine N	0.94	4.92	4.62	4.92
1 Azo Geranine 2G 2 Solway Blue BN 3 Lissamine Fast Yellow 2G	0.83	0.52	0.43	0.53
1 Azo Geranine 2G 2 Solway Blue BN 3 Tartrazine N	0.83	5.53	4.59	4.92
1 Lissamine Red 6B 2 Solway Blue A 3 Lissamine Fast Yellow 2G	0.50	0.53	0.27	0.21
1 Lissamine Red 6B 2 Solway Blue A 3 Tartrazine N	0.50	4.92	2.46	2.43
1 Lissamine Red 6B 2 Solway Blue BN 3 Lissamine Fast Yellow 2G	0.44	0.52	0.23	0.21
1 Lissamine Red 6B 2 Solway Blue BN 3 Tartrazine N	0.44	5.53	2.44	2.43
1 Lissamine Red 7BP 2 Solway Blue A 3 Lissamine Fast Yellow 2G	1.84	0.53	0.98	1.20
1 Lissamine Red 7BP 2 Solway Blue BN 3 Lissamine Fast Yellow 2G	2.77	0.52	1.44	1.20

* Gradients of the linear Q_1 versus Q_2 plots.

TABLE IV. Affinity Difference between Dyes—Calculated from Rates of Uptake from Infinite Dye Bath Using

Equation: $\frac{dQ_1}{dt} \Big/ \frac{dQ_2}{dt} = \frac{z_1}{z_2} \cdot \frac{C_{B_1}}{C_{B_2}} \cdot \frac{F_1}{F_2} \cdot e^{\frac{-(\Delta\mu_1 - \Delta\mu_2)}{RT}}$

i Mixture	ii $\frac{dQ_1}{dt} / \frac{dQ_2}{dt}$	iii $\frac{C_{B_1}}{C_{B_2}}$ (molar/molar)	iv $\frac{z_1}{z_2}$	v $\frac{F_1}{F_2}$	vi $e^{\frac{-(\Delta\mu_1 - \Delta\mu_2)}{RT}}$	vii $\frac{-(\Delta\mu_1 - \Delta\mu_2)}{RT}$	viii $-(\Delta\mu_1 - \Delta\mu_2)$ (kcal.)
1 Naphthalene Scarlet 4R 2 Solway Blue A	0.71	1.09	1.50	0.59	0.74	−0.31	−0.22
1 Naphthalene Scarlet 4R 2 Solway Blue BN	0.62	1.08	1.50	0.44	0.87	−0.14	−0.10
1 Naphthalene Scarlet 4R 2 Lissamine Fast Yellow 2B	0.26	0.82	1.50	0.78	0.27	−1.31	−0.91
1 Naphthalene Scarlet 4R 2 Tartrazine N	3.52	1.63	1.00	1.36	1.59	+0.46	+0.32
1 Azo Geranine 2G 2 Solway Blue A	0.94	0.63	1.00	0.97	1.54	+0.43	+0.30
1 Azo Geranine 2G 2 Solway Blue BN	0.83	0.62	1.00	0.72	1.86	+0.63	0.44
1 Azo Geranine 2G 2 Lissamine Fast Yellow 2G	0.53	0.47	1.00	1.27	0.89	−0.12	−0.08
1 Azo Geranine 2G 2 Tartrazine N	4.92	0.93	0.67	2.22	3.57	+1.27	+0.88
1 Lissamine Red 6B 2 Solway Blue A	0.50	0.81	1.00	0.36	1.71	+0.54	+0.37
1 Lissamine Red 6B 2 Solway Blue BN	0.44	0.80	1.00	0.27	2.04	+0.71	+0.49
1 Lissamine Red 6B 2 Lissamine Fast Yellow 2G	0.21	0.61	1.00	0.48	0.72	−0.34	−0.24
1 Lissamine Red 6B 2 Tartrazine N	2.43	1.21	0.67	0.83	3.63	+1.29	+0.89
1 Lissamine Red 7BP 2 Solway Blue A	1.84	0.78	1.00	0.24	9.83	+2.29	+1.58
1 Lissamine Red 7BP 2 Solway Blue BN	2.77	0.77	1.00	0.18	20.00	+3.00	+2.08
1 Lissamine Red 7BP 2 Lissamine Fast Yellow 2G	1.20	0.62	1.00	0.31	6.24	+1.83	+1.27
1 Solway Blue A 2 Lissamine Fast Yellow 2G	0.53	0.75	1.00	1.31	0.54	−0.62	−0.43
1 Solway Blue A 2 Tartrazine N	4.92	1.49	0.67	2.29	2.15	+0.77	+0.53
1 Solway Blue A 2 Naphthalene Fast Orange 2G	0.34	0.71	1.00	0.47	1.02	+0.02	+0.01
1 Solway Blue BN 2 Lissamine Fast Yellow 2G	0.52	0.76	1.00	1.75	0.39	−0.94	−0.65
1 Solway Blue BN 2 Tartrazine N	5.53	1.51	0.67	3.06	1.79	+0.59	+0.41
1 Solway Blue BN 2 Naphthalene Fast Orange 2G	0.29	0.72	1.00	0.63	0.64	−0.45	−0.31

TABLE V. Affinity Difference in kcal. between Dye Named in Column i and Solway Blue A

		Affinity differences estimated by competition with									
i	Direct competition ii	Lissamine Red 7BP iii	Lissamine Fast Yellow 2G iv	Lissamine Red 6B v	Azo Geranine 2G vi	Naphthalene Fast Orange 2G vii	Naphthalene Scarlet 4R viii	Tartrazine N ix	Average affinity difference x	Standard deviation (where significant) xi	Affinities (relative to tartrazine N=0) xii
Lissamine Red 7BP	+1.58		+1.70	*	*	*	*		+1.64	—	†+2.11
Lissamine Fast Yellow 2G	+0.43	+0.31		+0.61	+0.38	*	+0.69	*	+0.48	0.16	+0.96
Lissamine Red 6B	+0.37	*	+0.19		*	*	*	+0.36	+0.31	0.14	+0.90
Azo Geranine 2G	+0.30	*	+0.35	*		*	*	+0.35	+0.33	—	+0.83
Naphthalene Fast Orange 2G	−0.01	*	*	*	*	*	*	*	−0.01	—	+0.52
Solway Blue BN	*	−0.50	−0.22	−0.12	−0.14	−0.32	−0.12	−0.11	−0.22	0.15	+0.41
Naphthalene Scarlet 4R	−0.22	*	−0.48	*	*	*		−0.21	−0.30	0.15	+0.31
Tartrazine N	−0.53		*	−0.52	−0.58	*	−0.54	*	−0.54	—	0

* Measurements rendered impracticable by similarity of absorption spectra.
† Solway Blue A on this scale has an affinity of +0.53 kcal.

tory in view of the assumptions made, notably that of constant diffusion coefficients. On the basis of the foregoing argument, the affinity values calculated give the relative ability of the dyes to share the available dyeing sites in the fiber and a logical sequel to this is the comparison with affinities derived from other measurements. The affinities of this range of dyes have been determined by competition with chloride ions, using a desorption technique [2]. In this, chloride ions are allowed to compete for the available sites in the fiber, conditions being so chosen that the fiber is virtually saturated.

In Table VI, the differences in affinities relative to Solway Blue A are compared—as this is the simplest method of summarizing the data. The last column gives the differences in the relative affinities obtained from rate and desorption data.

Before attributing any significance to the differences in relative affinity shown in the last column, it is necessary to bear in mind the errors involved in the rate measurements, the use of diffusion coefficients based on Fick's law in deriving the affinities from kinetic data and the fact that the relative affinities determined by desorption represent a small fraction of the total affinity as measured by this technique (ranging from 6.6 kcal. for Lissamine Red 7BP to 4.7 kcal. for Solway Blue A). Since these affinity values are subject to an error of ±0.2 kcal., the error in the difference figures will be proportionately greater. In all cases the difference of affinity between the individual dyes and Solway

TABLE VI. Affinity Relative to Solway Blue A

Dye	From rate measurements	By desorption	Difference in relative affinity (desorption-rate)
Lissamine Red 7BP	+1.64	+1.73	+0.09
Lissamine Fast Yellow 2G	+0.48	+0.63	+0.15
Azo Geranine 2G	+0.33	+0.44	+0.11
Lissamine Fast Red 6B	+0.31	+0.70	+0.39
Naphthalene Fast Orange 2G	−0.01	+0.33	+0.34
Solway Blue BN	−0.22	+0.38	+0.60
Naphthalene Scarlet 4R	−0.30	+1.21	+1.51
Tartrazine N	−0.54	+0.33	+0.87

Blue A from desorption experiments is greater than the same difference deduced from this work.

With two dyes, Naphthalene Scarlet 4R and Tartrazine N, this difference is excessive and too large to be accounted for by experimental inaccuracies. Naphthalene Scarlet 4R is trisulphonated, and Tartrazine N is a disulphonated carboxylic acid and under the experimental conditions, both are effectively tribasic in contrast to the disulphonated Solway Blue A. The most revealing fact, however, is that by desorption the affinity of Naphthalene Scarlet 4R is considerably higher than that of Solway Blue A, whereas from the rate determinations its affinity is slightly lower. The same tendency is also present, to a marked degree, in the case of Tartrazine N. Thus it is apparent that these two dyes cannot compete with Solway Blue A for attachment to the fiber, to the extent which would be expected from their desorption affinities. That this anomalous behavior is not peculiar to the comparison with Solway Blue A is shown in Table VII, which has been compiled from Table IV.

In each case, the first dye in the mixture is dibasic and the second tribasic. In every mixture, the affinity of the tribasic dye determined by rate measurements is lower than that indicated by desorption measurements. Thus large anomalies arise when dyes of different degrees of sulphonation are in competition. The affinities derived from the kinetic data relied on the assumption that the external surface was saturated with dye, and since dye molecules are bulky entities, these are the very conditions under which deviations from stoichiometry between dye uptake and the number of amine end groups in the fiber are likely to occur. The desorption conditions are of relatively low saturation of dye, and a large number of chloride ions which because of their small size are presumably able to fill every amine group unoccupied by dye.

TABLE VII. Relative Affinities of Di- and Tribasic Dyes by Competition and Desorption

Mixture of dyes	Difference of affinity by: Desorption (kcal.)	Difference of affinity by: Competition (kcal.)	Discrepancy of affinity (competition-desorption)
Solway Blue BN Tartrazine N	+0.05	+0.41	+0.36
Lissamine Red 6B Tartrazine N	+0.37	+0.89	+0.52
Azo Geranine 2G Tartrazine N	+0.11	+0.88	+0.77
Lissamine Fast Yellow 2G Naphthalene Scarlet 4R	−0.58	+0.91	+1.49
Solway Blue A Naphthalene Scarlet 4R	−1.21	+0.22	+1.43
Solway Blue A Tartrazine N	−0.33	+0.53	+0.86

The competition between the chloride ions and the dye anions must, in the main, be ionic in nature and arise from displacement of the sulphonic acid group from the amine site. On the other hand, it is apparent that competition between two large organic molecules would occur not only in the neighborhood of the amine site, but also in those hydrophobic areas of the fiber to which the organic residues are attached. This argument suggests that it might be possible to displace a sulphonic acid group from its site by means of a chloride ion if the dye were, say, a trisulphonate, whereas this could not occur if the dye were a disulphonate. Thus, using the chloride ion for desorption would show the polysulphonated dyes to have a relatively larger affinity.

Another cause for the deviation must be discussed. In deriving the formula for the activity of the dye on the fiber, it was assumed that the amino group sides could be grouped [2]. By so doing, the stoichiometry of dyes with sulphonic acid groups differently disposed in the molecule was readily explained. However, if it is possible to group these sites z at a time, it is reasonable to suppose that the difficulties in grouping them will increase as the number in the group increases or as the condition of saturation is approached. This means that, in practice, the tri-basic dye will not be accommodated as easily as the dibasic, which in turn will be more difficult than the monobasic. Another way of saying this is that it is unlikely for the sulphonic acid groups to be adjacent to the charged amino groups, and hence on steric grounds it will be easier to accommodate the dyes of lower basicity. Explanations of this kind are not completely satisfactory, and much work is required to elucidate this very complex problem.

Conclusions and Summary

The work presented in this paper is an attempt to rationalize the dyeing of nylon when two dyes

are applied simultaneously. The rate of uptake data has been treated on the basis of a modified diffusion equation in which the rate of transfer of dye through the fiber is assumed to be proportional to the gradient of activity of the dyes. A logical deduction from this equation is that, under infinite dye bath conditions, the ratio of the rates of uptake of the two dyes will be independent of time but dependent upon the dye bath concentration, the diffusion coefficients of the dyes, their basicities, and their affinities for the fiber. The results obtained here have confirmed these deductions and affinity differences between pairs of dyes have been calculated. A comparison of these with results obtained by the techniques of desorption shows good agreement except where dyes of differing basicity are considered. In these cases, the conditions of almost complete saturation of the external surface of the fiber used here show up competition between dyes for the available sites, and discrepancies between affinities calculated on the basis of kinetic and desorption data can be accounted for by steric considerations.

The fact that constant uptake ratios may be obtained is in contrast with the excessive incompatibility which occurs with acid dyes in practice. The change of behavior must therefore be brought about by (*a*) the short liquor ratios and (*b*) the relatively low dye concentrations which are used in practical dyeing. The present work can therefore be regarded as an extreme case under which compatibility of dyes is the rule rather than the exception, and which can be taken as a starting point for a study of incompatibility of dyes under practical conditions. In this way it should be possible to explain some of the apparently anomalous results which occur, and by improving the understanding of such systems, to enable dyes to be selected on a rational basis for any given practical application.

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APPENDIX I

Determination of F/ρ^2 from Data for Single Dyes Applied from Infinite Dye Bath

Dye	t (min.)	C_B (g./liter)	Q (millimols/ kg. nylon)*	Est. equil. value (millimols/ kg. nylon)*	$t_{\frac{1}{2}}$ (sec.)	$\frac{F}{\rho^2}$ (sec.$^{-1}\times 10^5$)
Naphthalene Fast Orange 2GS	5	1.00	4.54	18.8	900	7.00
	15		8.52			
	30		13.64			
	60		14.07			
	120		18.76			
	300		18.66			
Solway Blue BNS	5	1.00	4.18	17.7	1440	4.38
	15		6.98			
	30		9.68			
	60		13.13			
	120		15.69			
	300		17.68			
Solway Blue AS	5	1.00	3.43	17.0	1920	3.28
	15		6.16			
	30		8.32			
	60		12.24			
	120		14.28			
	300		—			
Azo Geranine 2GS	5	1.00	2.66	18.1	1980	3.18
	15		5.53			
	30		8.54			
	60		12.35			
	120		15.84			
	300		17.82			
Lissamine Fast Yellow 2GS	5	1.00	4.25	19.9	2520	2.50
	15		5.37			
	30		7.38			
	60		10.91			
	120		15.51			
	300		17.22			
Naphthalene Scarlet 4RS	5	1.00	1.86	13.1	3240	1.94
	15		3.85			
	30		4.96			
	60		6.93			
	120		9.75			
	300		13.12			
Tartrazine NS	5	1.00	1.30	11.7	4310	1.43
	15		2.21			
	30		3.23			
	60		4.72			
	120		7.82			
	300		11.25			
Lissamine Red 6BS	5	1.00	2.44	19.7	5280	1.19
	15		3.95			
	30		5.43			
	60		8.10			
	120		11.35			
	300		16.75			
Lissamine Red 7BPS	5	1.00	1.92	23.9	8100	0.78
	15		3.29			
	30		5.98			
	60		7.25			
	120		10.46			
	300		18.88			

* These measurements were carried out at 75° C., using formic acid to produce a dye bath pH of 3.2.

APPENDIX II

Rate of Dyeing Data for Binary Mixtures from Infinite Dye Bath

Dye combination	C_{B_1}/C_{B_2} (molar/molar)	t (min.)	Q_1 (millimols/kg. nylon)*	Q_2 (millimols/kg. nylon)*	$\frac{dQ_1}{dt} / \frac{dQ_2}{dt}$ (Gradient of Q_1 vs. Q_2 plot)
		5	1.70	1.21	
		15	2.56	1.91	
(1) Lissamine Red 6B		30	3.62	2.85	
(2) Lissamine Fast	4.24	60	4.99	3.91	1.31
Yellow 2G		120	6.86	5.22	
		300	11.23	7.02	
		5	1.18	2.07	
		15	1.99	3.49	
		30	2.60	4.74	
do	1.81	60	3.22	6.14	0.49
		120	4.41	8.65	
		300	6.71	10.99	
		5	0.92	2.56	
		15	1.54	4.52	
		30	2.03	6.22	
do	1.01	60	2.55	8.10	0.32
		120	3.37	10.44	
		300	4.60	13.23	
		5	0.67	3.01	
		15	1.05	5.06	
		30	1.41	6.86	
do	0.605	60	1.82	9.10	0.20
		120	2.40	11.60	
		300	3.39	15.01	
		5	0.48	3.43	
		15	0.72	5.56	
		30	1.06	8.22	
do	0.363	60	1.31	10.63	0.12
		120	1.74	13.81	
		300	2.22	16.49	
		5	0.45	4.31	
		15	0.62	6.99	
		30	0.76	9.57	0.07
do	0.207	60	1.03	12.66	
		120	1.18	15.76	
		300	1.42	17.71	
		5	0.17	4.09	
		15	0.26	6.47	
		30	0.32	8.61	
do	0.086	60	0.37	11.72	0.03
		120	0.50	15.01	
		300	0.63	17.86	
		5	0.85	0.44	
		15	1.73	0.63	
(1) Tartrazine N		30	2.19	0.82	
(2) Lissamine Red 6B	7.43	60	3.22	1.10	3.56
		120	4.88	1.41	
		300	6.74	2.08	
		5	0.97	0.82	
		15	1.75	1.32	
		30	2.28	1.55	
do	3.31	60	3.12	2.14	1.64
		120	4.17	2.72	
		300	5.60	3.69	

* These dyeings were carried out at 75° C. from a dye bath whose pH was adjusted to 3.2 with formic acid.

Rate of Dyeing Data for Binary Mixtures from Infinite Dye Bath (Continued)

Dye combination	C_{B_1}/C_{B_2} (molar/molar)	t (min.)	Q_1 (millimols/kg. nylon)*	Q_2	$\frac{dQ_1}{dt} / \frac{dQ_2}{dt}$ (Gradient of Q_1 vs. Q_2 plot)
		5	0.86	1.02	
		15	1.46	1.66	
		30	1.86	2.04	
do	1.93	60	2.55	2.68	0.97
		120	3.63	3.82	
		300	5.33	5.81	
		2	2.82	0.28	
		5	4.81	0.38	
(1) Naphthalene Fast		10	6.66	0.42	
Orange 2G	12.42	20	9.41	0.49	29.5
(2) Solway Blue BN		40	12.43	0.55	
		60	—	—	
		2	2.79	0.46	
		5	5.08	0.72	
		10	6.22	0.77	
do	2.07	20	8.42	0.97	11.4
		40	11.62	1.22	
		60	11.97	1.53	
		2	2.13	0.44	
		5	3.28	0.65	
		10	4.99	1.06	
do	1.38	20	7.09	1.44	5.65
		40	9.37	1.76	
		60	11.68	2.14	
		2	1.46	0.65	
		5	2.34	1.02	
		10	3.24	1.45	
do	0.92	20	4.33	1.87	2.57
		40	6.63	2.66	
		60	8.64	3.43	
		2	1.37	0.95	
		5	2.22	1.52	
(1) Naphthalene Fast		10	2.78	2.16	
Orange 2G	0.46	20	4.00	3.02	1.46
(2) Solway Blue BN		40	5.77	3.82	
		60	6.66	4.41	
		2	0.75	1.45	
		5	0.98	2.21	
		10	1.34	3.18	
do	0.15	20	1.87	4.68	0.35
		40	2.70	6.53	
		60	3.11	8.07	
		2	2.39	0	
(1) Naphthalene Fast		5	4.14	0.06	
Orange 2G		10	5.85	0.08	
(2) Lissamine	14.33	20	7.76	0.11	100
Violet AV		40	11.20	0.19	
(C.I. No. 53)		60	—	—	
		2	2.45	0.23	
		5	4.11	0.36	
		10	5.62	0.43	
do	4.78	20	7.80	0.51	17.2
		40	10.95	0.71	
		60	—	—	

Rate of Dyeing Data for Binary Mixtures from Infinite Dye Bath (Continued)

Dye combination	C_{B_1}/C_{B_2} (molar/molar)	t (min.)	Q_1 (millimols/kg. nylon)*	Q_2	$\frac{dQ_1}{dt} / \frac{dQ_2}{dt}$ (Gradient of Q_1 vs. Q_2 plot)
		2	2.39	0.52	
		5	3.70	0.67	
		10	5.58	0.93	
do	2.39	20	7.14	1.11	7.91
		40	10.56	1.52	
		60	12.13	1.71	
		2	2.30	0.66	
		5	3.65	0.96	
		10	5.34	1.32	
do	1.59	20	7.32	1.55	4.95
		40	9.90	1.98	
		60	11.75	2.43	
		2	1.93	0.81	
		5	3.11	1.19	
		10	4.09	1.44	
do	1.06	20	6.21	2.02	3.60
		40	8.08	2.44	
		60	9.56	2.65	
		2	1.42	1.07	
(1) Naphthalene Fast		5	2.40	1.64	
Orange 2G		10	3.32	2.21	
(2) Lissamine	0.53	20	4.56	2.86	1.98
Violet AV		40	6.16	3.51	
		60	7.52	4.10	
		2	0.77	1.65	
		5	1.31	2.61	
		10	1.67	3.02	
do	0.18	20	2.34	4.13	0.71
		40	3.19	4.92	
		60	3.82	5.82	
		2	0.84	0.90	
		5	1.26	1.44	
(1) Naphthalene		10	1.70	1.96	
Scarlet 4R	1.09	20	2.30	2.99	0.71
(2) Solway Blue A		40	3.30	4.25	
		60	3.49	5.13	
		2	0.74	0.88	
		5	1.14	1.56	
(1) Naphthalene		10	1.56	2.31	
Scarlet 4R	1.08	20	2.12	3.10	0.62
(2) Solway Blue BN		40	2.86	4.40	
		60	3.38	5.14	
		2	0.57	1.79	
(1) Naphthalene		5	1.05	2.98	
Scarlet 4R		10	1.18	3.71	
(2) Lissamine Fast	0.82	20	1.59	5.22	0.26
Yellow 2G		40	2.00	6.75	
		60	2.16	7.55	
		2	0.86	0.31	
		5	1.52	0.43	
(1) Naphthalene		10	1.91	0.57	
Scarlet 4R	1.63	20	2.52	0.76	3.52
(2) Tartrazine N		40	3.19	0.96	
		60	3.87	1.14	

Rate of Dyeing Data for Binary Mixtures from Infinite Dye Bath (Continued)

Dye combination	C_{B_1}/C_{B_2} (molar/molar)	t (min.)	Q_1 (millimols/kg. nylon)*	Q_2	$\frac{dQ_1}{dt} / \frac{dQ_2}{dt}$ (Gradient of Q_1 vs. Q_2 plot)
		2	1.07	0.81	
		5	1.80	1.34	
(1) Azo Geranine 2G		10	2.49	2.23	
(2) Solway Blue A	0.63	20	3.52	3.30	0.94
		40	4.88	4.75	
		60	5.85	5.83	
		2	0.83	0.92	
		5	1.41	1.52	
(1) Azo Geranine 2G		10	1.85	2.18	
(2) Solway Blue BN	0.62	20	2.58	2.98	0.83
		40	3.44	4.01	
		60	3.89	4.67	
		2	0.74	1.40	
		5	1.19	2.10	
(1) Azo Geranine 2G		10	1.59	2.85	
(2) Lissamine Fast	0.47	20	2.08	3.83	0.53
Yellow 2G		40	2.73	4.99	
		60	3.27	5.79	
		2	1.35	0.24	
		5	2.08	0.45	
(1) Azo Geranine 2G		10	2.86	0.46	
(2) Tartrazine N	0.93	20	3.89	0.69	4.92
		40	5.14	0.98	
		60	5.72	1.19	
		2	0.54	0.90	
		5	0.97	1.72	
(1) Lissamine Red 6B		10	1.41	2.57	
(2) Solway Blue A	0.81	20	1.93	3.82	0.50
		40	2.65	5.47	
		60	3.38	6.68	
		2	0.55	0.99	
		5	0.86	1.62	
(1) Lissamine Red 6B		10	1.21	2.47	
(2) Solway Blue BN	0.80	20	1.70	3.55	0.44
		40	2.25	4.85	
		60	2.60	5.61	
		2	0.54	2.01	
		5	0.70	3.11	
(1) Lissamine Red 6B		10	0.94	4.09	
(2) Lissamine Fast	0.61	20	1.24	5.64	0.21
Yellow 2G		40	1.55	7.30	
		60	1.83	8.51	
		2	0.86	0.39	
		5	1.24	0.51	
(1) Lissamine Red 6B		10	1.66	0.70	
(2) Tartrazine N	1.21	20	2.26	1.02	2.43
		40	3.10	1.38	
		60	3.72	1.54	
		2	1.01	0.39	
		5	1.58	0.68	
(1) Lissamine Red 7BP		10	2.26	1.08	
(2) Solway Blue A	0.78	20	3.03	1.46	1.84
		40	4.16	1.94	
		60	5.08	2.54	

Rate of Dyeing Data for Binary Mixtures from Infinite Dye Bath (Continued)

Dye combination	C_{B_1}/C_{B_2} (molar/molar)	t (min.)	Q_1 (millimols/kg. nylon)*	Q_2	$\frac{dQ_1}{dt} / \frac{dQ_2}{dt}$ (Gradient of Q_1 vs. Q_2 plot)
		2	1.15	0.40	
		5	1.80	0.56	
(1) Lissamine Red 7BP		10	2.45	0.86	
(2) Solway Blue BN	0.77	20	3.26	1.22	2.77
		40	4.51	1.62	
		60	5.48	1.93	
		2	1.22	1.06	
		5	1.85	1.54	
(1) Lissamine Red 7BP		10	2.41	1.88	
(2) Lissamine Fast Yellow 2G	0.62	20	3.10	2.60	1.20
		40	4.18	3.42	
		60	4.64	3.86	
		2	0.64	1.86	
		5	1.01	2.87	
(1) Solway Blue A		10	1.45	3.91	
(2) Lissamine Fast Yellow 2G	0.75	20	2.32	5.28	0.53
		40	3.05	6.96	
		60	3.87	7.99	
		2	1.14	0.30	
		5	2.02	0.39	
(1) Solway Blue A		10	3.18	0.57	
(2) Tartrazine N	1.49	20	4.60	0.78	4.92
		40	6.27	1.20	
		60	7.68	1.37	
		2	0.62	2.26	
		5	0.94	3.34	
(1) Solway Blue A		10	1.42	4.74	
(2) Naphthalene Fast Orange 2G	0.71	20	2.13	6.77	0.34
		40	2.81	8.97	
		60	3.15	10.17	
		2	0.82	1.83	
		5	1.25	2.78	
(1) Solway Blue BN		10	1.84	3.74	
(2) Lissamine Fast Yellow 2G	0.76	20	2.33	4.70	0.52
		40	3.14	6.27	
		60	3.68	7.34	
		2	1.33	0.44	
		5	2.32	0.66	
(1) Solway Blue BN		10	3.40	0.76	
(2) Tartrazine N	1.51	20	4.84	1.02	5.53
		40	6.53	1.26	
		60	7.36	1.73	
		2	0.62	2.13	
		5	1.00	3.37	
(1) Solway Blue BN		10	1.51	4.66	
(2) Naphthalene Fast Orange 2G	0.72	20	1.87	6.42	0.29
		40	2.47	8.67	
		60	2.92	10.12	

The Cellulose–Sodium Hydroxide–Water System in the Cyanoethylation of Cotton Cellulose[1]

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Abstract

When cotton is cyanoethylated with a large excess of acrylonitrile in the presence of aqueous alkali at fixed time and temperature, the extent of cyanoethylation and by-product formation is controlled by the ratios of cellulose, sodium hydroxide, and water employed. The mechanical restraints offered by the yarn and fabric structures alter these optimum conditions as well as the extent of cyanoethylation which takes place. Cyanoethylated cottons, having essentially equal nitrogen contents but different properties, can be prepared from a large number of compositions of cellulose, sodium hydroxide, and water. High sodium hydroxide contents in the starting mixtures result in substantial conversion to carboxyethyl groups with a subsequent loss of resistance to microbiological attack.

IN a previous publication from this Laboratory [5], the amount of cyanoethyl substitution in cotton in the presence of a large excess of acrylonitrile was shown to be related to the sodium hydroxide : cellulose ratio in the sample. Subsequent attempts to arrive at an optimum ratio of sodium hydroxide to cellulose failed when various concentrations of aqueous sodium hydroxide were employed. However, further examination of the data disclosed that water, in addition to cellulose and sodium hydroxide, must be considered in order to clearly define this optimum ratio. This type of three-component system has been used by other workers in the field of cellulose. D'Ans and Jäger [2], and Hess and co-workers [7], employed three-component diagrams (cellulose-sodium hydroxide-water) to study cellulose complexes in aqueous sodium hydroxide, and Miles and his co-workers [9, 10] clearly delineated areas of swelling and solution of cellulose and cellulose nitrate during nitration by using a three-component plot comprising sulfuric acid, nitric acid, and water, in which points of identical nitrogen content were connected to form patterns. Such an approach was found applicable to a study of the cyanoethylation of cotton cellulose with a large excess of acrylonitrile in the presence of aqueous bases.

[1] This paper was delivered in part at the Gordon Research Conference on Textiles, New London, New Hampshire, July 9–13, 1956.

[2] One of the Laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

Methods and Materials

For convenience the cotton used in these experiments was in two forms : an oxford weave tape with 120 warp ends and 44 filling picks, 1 in. wide, 0.2 oz./linear yard ; and a commercial cheesecloth. Both fabrics were scoured and bleached before use. The acrylonitrile was of commercial grade, prepared from hydrogen cyanide and acetylene, and contained 0.7% water. Where lower water concentrations were required, the acrylonitrile was dried over anhydrous calcium sulfate to 0.06% water content. Nitrogen analyses were carried out by the Kjeldahl method, and water was determined by titration with Karl Fischer reagent. Analyses for β, β'-oxydipropionitrile, ethylene cyanohydrin, and acrylonitrile were conducted by an infrared absorption method developed in this Laboratory [4]. Iodine adsorptions were carried out by the method of Hessler and Power [8], and soil-burial tests followed the method described by Dean *et al.* [3]. Carboxyethyl determinations were carried out by soaking the samples in dilute acid to convert to the acid form, washing with distilled water, treating with excess standard sodium hydroxide, and back-titrating with standard acid to the phenolphthalein end point.

Cotton tapes or cheesecloth were cut to approxi-

mately 1.6 g., weighed accurately, and the weight corrected for moisture content. This corrected weight is referred to hereafter as "cellulose." The cotton was immersed in aqueous sodium hydroxide containing a small amount of wetting agent, squeezed between rolls, and weighed. The length of time in the alkali within the limits studied had no effect on the results obtained. Samples immersed for 5 sec. resulted in the same substitution as those soaked for 20 hr., provided the cellulose-sodium hydroxide-water ratios were identical. When higher water contents were desired, water was added to the acrylonitrile. Previous experiments had demonstrated that such practice was permissible, provided the solubility limit of water in the acrylonitrile was not exceeded. In fact, it is mandatory that all water in the system be included in the calculations. After weighing, the padded samples were dropped into 250-ml. round-bottom flasks containing 100 ml. (80 g.) of preheated acrylonitrile. These flasks were clamped in a "wrist-action" shaking machine with the body of the flask immersed in the water of a constant-temperature bath. All cyanoethylations were carried out for ½ hr. at 60° C. At the end of the reaction time the flask was removed from the bath, the cotton was removed from the reactor flask and dropped into a measured volume of standard acid. After standing for about an hour, the cotton samples were back-titrated with standard base to determine the amount of sodium hydroxide retained on the tape. Samples of the acrylonitrile phase were removed for infrared and Karl Fischer analyses, and water was added to the remainder which was then titrated to the phenolphthalein end point with standard acid. The alkali present on the tape and in the acrylonitrile was thus determined separately.

No attempt was made to study commercial procedures using acrylonitrile containing 3.5% water and with acrylonitrile to cellulose ratios of less than 10:1, since the simple shaker employed could not prevent the formation of two layers once the acrylonitrile had become saturated with water.

To obtain the substitution patterns shown in subsequent figures, points were plotted in triangular coordinates, with respect to the relative ratios of cellulose, total sodium hydroxide, and total water in the system; and the nitrogen content of the sample inserted next to the point. These nitrogen contents were not corrected for moisture content, since such corrections would increase the nitrogen value only slightly and would in no way affect the conclusions to be drawn. Although approximately 150 samples were utilized in drawing the pattern derived from the cotton tape, the construction of the pattern was facilitated by adapting a method suggested by Grinsfelder [6]. This adaptation consisted of drawing arbitrary straight lines through convenient groups of points on the original plot. The points lying along these lines were then replotted on rectangular coordinates using per cent N versus per cent sodium hydroxide. A smooth curve was drawn through the points from each arbitrary straight line. From the family of curves thus produced, values of NaOH for each whole number per cent N were obtained, from which the triangular plots shown were drawn.

Results

Figure 1 shows the pattern obtained using cotton tapes. The maximum substitution, slightly over 11% N (2.25 cyanoethyl groups per anhydroglucose unit), was obtained with 32% cellulose, 3% sodium hydroxide, and 65% water.

If patterns such as Figure 1 are used to predict the results of cyanoethylations, further complications arise from the initiation of mercerization at sufficiently high concentrations of the aqueous alkali and by the mechanical restraints offered by the yarn and fabric structure. Samples of the cotton tape and cheesecloth were allowed to soak overnight in solutions of 2 to 25% NaOH, blotted to remove the excess adhering solution [11], weighed, and titrated. Table I gives the results obtained.

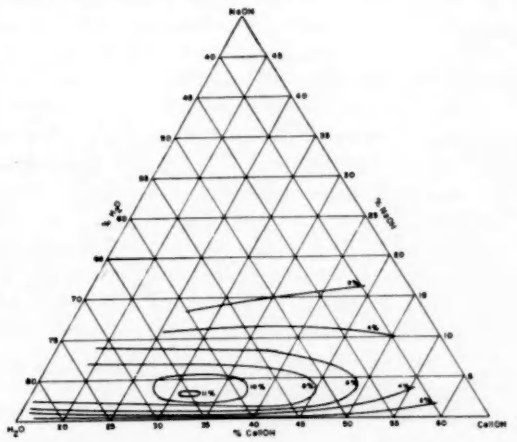

Fig. 1. Nitrogen contents of cotton tapes cyanoethylated in the presence of aqueous sodium hydroxide.

TABLE I. Absorption of Aqueous Sodium Hydroxide by Cotton Tape and Cheesecloth

Concentration % NaOH	Composition of sample					
	Tape			Cheesecloth		
	% CellOH	% NaOH	% H_2O	% CellOH	% NaOH	% H_2O
2	58.9	1.7	39.4	56.4	1.6	42.0
4	57.9	2.5	39.6	55.2	2.5	42.3
6	56.4	4.1	39.5	54.1	4.2	41.7
8	55.1	5.1	39.8	51.0	5.3	43.7
10	51.5	7.4	41.1	37.2	8.5	54.3
12	47.5	9.5	43.0	33.1	11.1	55.8
15	45.3	12.2	42.5	30.7	13.6	55.7
17	43.7	13.8	42.5	29.7	15.2	55.0
20	42.7	16.1	41.2	29.4	17.6	53.0
25	42.2	19.6	38.1	28.4	21.6	49.9

It can be seen that between NaOH concentrations of 8 and 10% the water content of the cheesecloth increases rapidly, whereas the water content of the tape increases only slightly. This can be attributed to the difference in swelling limitations imposed on the samples by their respective fabric structures, and agrees almost quantitatively with the data of Coward and Spencer [1], who centrifuged alkali-treated cotton tapes and lint cotton.

The pattern derived from cheesecloth, similarly padded with NaOH and cyanoethylated under the same conditions as those used for tapes, is shown in Figure 2. It can be seen easily that the area of highest substitution is much higher than, and to the left of, the corresponding area for cotton tape. When molecular ratios are considered, the highest substitution area for tape is represented by an anhydroglucose–sodium hydroxide–water molar ratio of 1:0.38:18.2, while that for cheesecloth is 1:0.90:22.3. These ratios are based on total material initially present, however, and not on the composition of the cotton sample after reaction. At the point of highest substitution, the cotton tape retained only about 70% of the initial NaOH, while cheesecloth retained about 85%. Curves derived by connecting points of equal retention of sodium hydroxide follow the general contours of the substitution curves and their value diminishes with increasing water content. The pattern for sodium hydroxide retained on the tapes is shown in Figure 3, which includes the area of maximum substitution; it also includes a line designating the composition of acrylonitrile saturated with

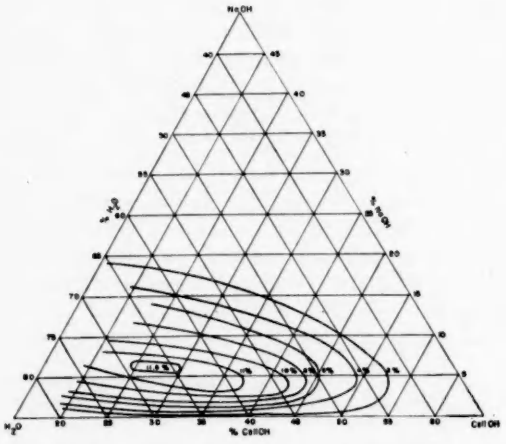

Fig. 2. Nitrogen contents of cotton cheesecloth cyanoethylated in the presence of aqueous sodium hydroxide.

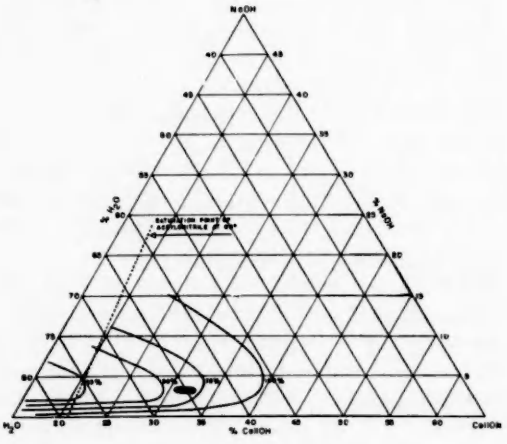

Fig. 3. Retention of sodium hydroxide by cotton tapes during cyanoethylation.

water in the quantities used in these studies. It can be seen that as substitution of the cellulosic hydroxyls increases, the amount of sodium hydroxide retained diminishes, since the number of reactive sites on the cellulose chain has been decreased. Similarly, as the amount of water in the mixture increases, more sodium hydroxide is extracted from the cotton. The net result of these influences is the family of curves shown in Figure 3.

Similarly, attempts to determine the fate of the water in the system proved impracticable due to the scatter of the points. Analyses of water in the acrylonitrile phase by the Karl Fischer method and subsequent calculations failed to detect a pattern for the distribution of water.

Acrylonitrile in the presence of bases is hydrated to ethylene cyanohydrin and β, β'-oxydipropionitrile. In addition, the polymerization of acrylonitrile is catalyzed by bases to yield highly colored products [12]. All of these side reactions are assumed to take place during the cyanoethylation of cotton cellulose. Unfortunately, the large volume of acrylonitrile used in these experiments prevented full application of the infrared technique. The small amounts of ethylene cyanohydrin (0 to 2%) and the large amounts of acrylonitrile (95 to 100% of the final mixture) made a complete material balance impossible. Ratios of acrylonitrile to cellulose used commercially should result in much higher by-product content and this method would then become applicable. On the other hand, even in the dilutions employed in these experiments the production of β, β'-oxydipropionitrile (up to 7% of the final mixture) was appreciable, and the pattern shown in Figure 4 was derived by the methods described. It is obvious that the amount of β, β'-oxydipropionitrile increases when the water or sodium hydroxide content of the system increases, particularly in areas in which the solubility of water in acrylonitrile is not exceeded.

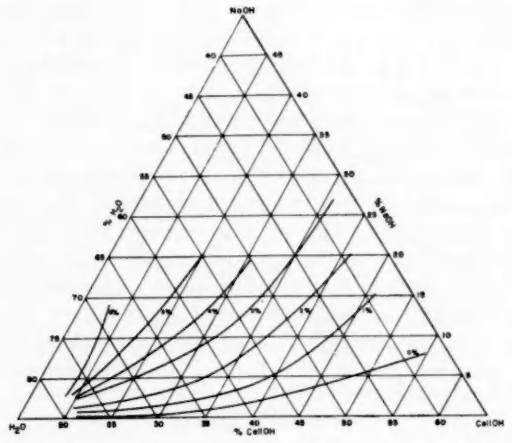

Fig. 4. Production of β, β'-oxydipropionitrile during the cyanoethylation of cotton tapes. The values shown represent concentration in weight per cent of the ether in the final acrylonitrile phase.

From Figure 1 it can be seen that cyanoethylated cottons, having essentially identical nitrogen contents, can be prepared from a large number of compositions of cellulose, sodium hydroxide and water. Four such samples, prepared from a 12/5 cotton sewing thread, and having substantially the same nitrogen content, were subjected to a soil-burial test. The original compositions and the time required for the samples to be destroyed are given in Table II.

TABLE II. Rot Resistance of Cyanoethylated Cottons Having Equal Nitrogen Contents

Sample	% N	Original composition % CellOH	% NaOH	% H_2O	Time to reach zero strength (weeks)
A	5.5	25	1	74	>12
B	5.5	54	2	44	>12
C	5.0	42	6	52	2
D	5.2	36	10	54	2

From the observed results it was believed that the samples containing higher amounts of sodium hydroxide were rendered more accessible to microbiological attack due to increased chemical accessibility or decreased crystallinity. Measurements by iodine adsorption [8] showed that the samples had accessibilities between 60 and 80% with no apparent relationship between the observed values and the amount of sodium hydroxide present in the starting mixture. However, further examination disclosed that carboxyethyl groups were present in all samples, but predominately in those which decomposed rapidly on soil burial. Samples "A" and "B" contained five carboxyethyl groups per thousand anhydroglucose units, while "C" and "D" had five per hundred units.

Previously cyanoethylated cotton tapes were reexamined and analyzed for carboxyethyl content. The results are shown in Table III, together with the results obtained on soil burial in a bed which decomposed control tapes in 10 days.

TABLE III. Carboxyethyl Contents and Rot Resistance of Cyanoethylated Cotton Tapes

Original composition			Analyses of product			
% CellOH	% NaOH	% H_2O	% N	Carboxyethyl groups per glucose unit	Cyanoethyl groups per glucose unit	Time to decompose (weeks)
51.8	5.1	43.1	6.2	0.010	0.95	4
44.8	11.3	43.9	4.7	0.042	0.65	2.5
21.3	1.9	76.7	4.5	0.004	0.65	>8
20.0	4.6	75.4	8.9	0.015	1.55	>8
19.1	5.6	75.2	6.8	0.040	1.05	2.5

From these data it appears that during the cyanoethylation reaction, some of the CN groups are hydrolyzed to COOH, producing carboxyethyl cellulose. It is postulated that in the presence of the aqueous alkali used as catalyst, these carboxyethyl groups bring about intense swelling of the cellulose with attendant decrease in crystallinity or increase in accessibility. This increase in chemical accessibility requires higher cyanoethyl substitution to protect the exposed anhydroglucose units from microbiological attack. For example, the tape sample containing 6.2% N and one carboxyethyl group per 100 glucose units was destroyed in 4 weeks, while the sample with 6.8% N and four carboxyethyl groups per 100 glucose units reached zero strength in 2.5 weeks. On the other hand, 8.9% N was sufficient to protect a sample containing 1.5 carboxyethyl groups per 100 glucose units.

Discussion

From the results it is apparent that the extent of cyanoethylation and by-product formation in the presence of a large excess of acrylonitrile at fixed time and temperature is controlled by the ratios of cellulose, sodium hydroxide, and water employed. High cyanoethyl substitution and low production of β, β'-oxydipropionitrile can be achieved by utilizing minimum amounts of sodium hydroxide and water in the reaction mixture.

The results of the soil-burial test show that the ratios of the components in the cellulose-sodium hydroxide-water system are most important. Perhaps the most interesting property of cyanoethylated cotton is its resistance to microbiological attack, and yet the swelling associated with as little as one carboxyethyl group per 100 anhydroglucose units is sufficient to bring about the destruction of a sample containing almost twice as much nitrogen as is normally required for protection. Higher contents of sodium hydroxide in the starting mixture produce higher amounts of carboxyethyl groups. No difference could be found between samples containing the same proportion of sodium hydroxide but different proportions of water, provided the sodium hydroxide content was low. Thus the least swelling of cyanoethylated cotton is obtained in samples prepared from mixtures containing low proportions of sodium hydroxide, regardless of the water content.

Conclusions

From the data presented it is concluded (1) that in order to clearly define the optimum conditions for the cyanoethylation of cotton cellulose in the presence of a large excess of acrylonitrile, account must be taken of the ratios of the three components, cellulose, sodium hydroxide, and water; (2) that the mechanical restraints offered by the yarn and fabric structures alter these optimum conditions as well as the extent of cyanoethylation which takes place; (3) that cyanoethylated cottons, having essentially the same nitrogen contents but different properties, can be prepared from a large number of compositions of cellulose, sodium hydroxide, and water; (4) that high sodium hydroxide contents in the starting mixture produce high carboxyethyl substitution in the product with attendant loss of resistance to soil burial; and (5) that minimum production of one of the by-products, namely, β, β'-oxydipropionitrile, is achieved with minimum water content in the system.

Since the ratios of cellulose, alkali, and water employed in this study are not those ordinarily employed commercially, it is not certain how far these conclusions can be extended to commercial practice.

Acknowledgment

Appreciation is expressed to Julian F. Jurgens for the many nitrogen determinations conducted in conjunction with this study.

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The Effect of Twist on the Static Modulus of Cotton Hawser-Twist Cord

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THE importance of twist in determining the extensibility of yarns and cords was recognized by Dyson [1]. Considerable work was done by Tipton [2] and others in measuring the dynamic modulus of finished cords. However, quantitative data on the relative effects of twist in the singles, ply, and cord appear to be lacking. This report presents the results of an empirical approach to delineate the relative effects of twist upon the modulus of cotton hawser-twist cord of a single construction. The analysis was made on the data obtained on a series of 54 cords of 16's/4/3 construction with ZZS twist, representing all the possible twist combinations with the nominal twists (before stretching) shown in Table I.

The cords were made from a single lot of Stoneville 2B cotton and were wet-stretched under a 12-lb. load. It is assumed that the twists and their associated effects were the only variables.

The test data were obtained with an Instron Tensile Tester,[2] with all tests conducted under standard atmospheric conditions of 65% relative humidity and 70° F. Five specimens were tested from each sample. The cords were strained at a rate of 8%/min. and cycled between load limits of 1 and 2.6 lb. (approximately 10% of the breaking load) for 20 cycles and then loaded to rupture. Because of the low rate of loading the moduli may be considered as having been determined for all practical purposes under static conditions.

The moduli were obtained by measuring the slopes of the rupture curves at the 10-lb. point. Actually, the tangents at these points were usually taken since the stress-strain curves of the cords were complex

TABLE I

Singles twist multiplier	Ply (t.p.i.)	Cord (t.p.i.)
2.65	18.6	10.2
3.05	19.2	11.1
3.45	19.8	12.0
	20.4	
	21.9	
	22.7	

[1] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

[2] Mention of the names of firms or trade products does not imply that they are endorsed or recommended by the U.S. Department of Agriculture over other firms or similar products not mentioned.

and not strictly linear. The 10-lb. point, which corresponded to approximately 40% of the breaking load, was chosen somewhat arbitrarily as experience had indicated that cycling cord to 2.6 lb. has little if any effect upon the slope of the extensibility curves at 10 lb. It should be further noted that the 10-lb. point is below the 12-lb. wet-stretching load. The moduli were expressed as grams per grex.

For most accurate analysis of the effect of twist on the moduli, the actual twists in the samples should be used. Although twist is readily counted in ply and cord constructions, it is difficult to count accurately in singles cotton yarn. Therefore, for the singles yarn, the nominal twists were used as calculated from the following formula:

$$\text{Nominal singles twist (t.p.i.)} = \text{twist multiplier} \times \sqrt{\text{yarn number}}.$$

The ply and cord twists were measured by use of a Suter twist tester. In performing the tests, twist was added to the ply while it was being removed from the cord, thus bringing the plies more nearly to their twist value before the cord twist was inserted. The values subsequently obtained for the plies therefore approximated their nominal values and were comparable with the singles and cord twists.

The moduli for the different cords ranged from 21.6 to 30.6 g./grex and appeared to be inversely correlated with twist regardless of whether the twist was in the singles, ply, or cord. A linear multiple-correlation analysis was made to determine the significance of the correlation between twist and modulus and the relative contributions of the constituent twists. The correlation coefficient of the multiple regression was found to be a highly significant 0.95 with a standard error of estimate of 0.67 g./grex. The regression equation derived was

$$Y = 70.23 - 1.070\,X_1 - 0.872\,X_2 - 1.445\,X_3$$

where

Y = Modulus, grams/grex
X_1 = Nominal singles twist, turns/inch
X_2 = Ply twist before cabling, turns/inch
X_3 = Cord twist, turns/inch

For this series of cords the regression coefficients proved to be significantly different. The cord twist had the greatest influence and the ply the least on the moduli.

To show the "goodness of fit" of the experimental data to a linear regression line, the observed values of twist were substituted in the multiple regression equation and the moduli calculated. In Figure 1 these values are plotted against the observed values for all of the cords. Although some slight departure from linearity is observed in the upper portion of the curve, this trend did not appear to be of sufficient magnitude to warrant a more complex analysis.

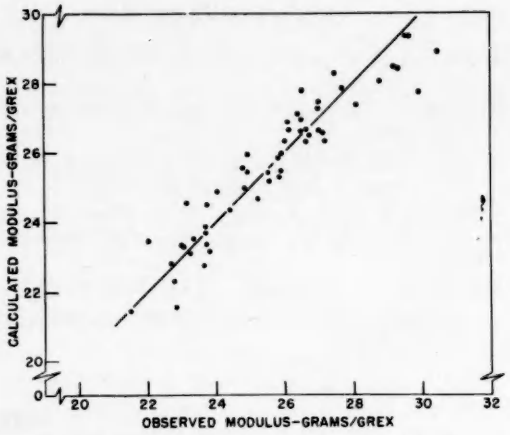

Fig. 1. Calculated versus observed moduli of 16's/4/3 ZZS cord.

Increasing the twist 1 t.p.i. in the components of this series of cords appeared to lower the modulus approximately 1 g./grex/t.p.i. if in either the singles or ply, and 1.5 g./grex/t.p.i. if in the cord. Although the absolute magnitude of the effect on the modulus might be expected to change with different cottons and processing organizations, its relative values are probably applicable to 16's/4/3 hawser-twisted cord. It seems likely that increasing the twist in any component will result in decreasing the modulus of cords of other constructions although the relative effects should be evaluated for the particular construction.

Acknowledgments

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Fluorine and Iodine Compounds as Flame Retardants for Cotton[1]

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Abstract

Fluorine and iodine compounds, both organic and inorganic, were tested as flame retardants for cotton. Comparison with bromine and chlorine compounds showed that the effectiveness of the halogens, on an equal weight basis, increases in the order: fluorine, chlorine, bromine, iodine, with the last two about equally effective.

IN the investigation of durable flame-retardant finishes for cotton fabrics conducted at the Southern Regional Research Laboratory, several classes of agents were studied, including organic polymers containing phosphorus and halogen. Of these, the polymers containing phosphorus and bromine have received the most attention [3, 8]. The substitution of chlorine for bromine in these polymers has been found to result in reduced effectiveness [6, 8]. But even with bromine, 20% added weight to the fabric is usually required for good results. In the hope of reducing the required weight add-on, the remaining two common halogens have been tried as substitutes for bromine.

Fluorine-containing compounds have been reported to be flame retardants [1, 4] and appeared attractive because the low atomic weight of fluorine might make possible the use of lower add-ons. On the other hand, preliminary tests showed that iodine might possess a high effectiveness even with its high atomic weight.

The object of the present investigation was to determine whether fluorine and iodine compounds, particularly when also containing phosphorus, showed promise as effective flame retardants for cotton at low add-ons. The method used was to test inorganic and organic compounds containing these halogens by comparing the flame resistance obtained with that from similar compounds containing bromine and chlorine.

Experimental

Inorganic Halides

The effectiveness of inorganic halides was judged from the minimum add-on necessary to impart flame resistance to 8-oz. cotton twill. Ammonium, lithium, magnesium, and zinc halides were tested, because these cations as the chlorides or bromides have been reported to be flame retardants for cotton [2, 6]. For the purpose of this comparison, fabric was considered flame-resistant when a char length of less than 10 in. was obtained in the Vertical Flame Test [7].

Soluble halides were applied to the fabric by impregnation with a water solution of the salt by means of squeeze rolls, followed by oven drying (110° C. for 30 min.) in a horizontal position on pin-frames. Samples were weighed after cooling in a desiccator to determine the add-on of halide. A range of add-ons was obtained by varying the concentration of the treating solution.

None of the fluorides used was soluble enough for this method of application. Instead a two-bath precipitation procedure was followed. Fabric samples were impregnated with a solution of a soluble salt of the metal, dried, and then treated with a solution of a fluoride to precipitate the desired insoluble fluoride on the fabric. After drying, samples were

[1] This is a report on one phase of a program of research on the flame-resistance treatment of cotton textiles, being supported at the Southern Utilization Research Branch by funds supplied by the Office of the Quartermaster General, Department of the Army, and conducted under the general supervision of the Research and Development Center, Natick, Massachusetts.

[2] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

rinsed in water to remove remaining soluble salts and finally redried and weighed as before. The add-ons measured by weight gain were spot checked by chemical analysis for fluorine. Maximum difference between add-ons determined by weight gain and analysis was 4%.

The add-ons of inorganic halides required for flame resistance are shown in Table I.

Organic Halides

The effectiveness of nonionic fluorine and iodine as flame retardants was tested in organic polymers containing phosphorus. Such polymers were synthesized and compared with triallyl phosphate polymers, one brominated and one unhalogenated. The brominated polymer, containing 35 to 40% bromine, is a very good flame retardant for cotton, while the unhalogenated polymer is relatively poor [8]. Only polymeric materials were considered, as previous experience showed that they were better flame retardants than their monomers.

Phosphorus-fluorine polymer. A mixed allyl-trifluoroethyl phosphate was synthesized and polymerized to a product containing phosphorus and fluorine. The preparation of the polymer was accomplished in the following manner.

A solution of 120 g. (1.2 mole) 2,2,2-trifluoroethanol and 95 g. (1.2 mole) pyridine was added dropwise to a well-stirred mixture of 92 g. (0.6 mole) phosphoryl chloride and 150 ml. toluene. The reaction was conducted at 0–10° C. in an apparatus protected from atmospheric moisture. After addition was complete the mixture was stirred for 1 hr. at room temperature. The pyridine hydrochloride was removed by filtration through a fritted glass filter, and the filtrate added dropwise to 35 g. (0.6 mole) allyl alcohol and 50 ml. toluene, using the same conditions as in the previous addition. After standing overnight, the mixture was filtered. The solvent was evaporated from the filtrate under vacuum and the residue vacuum distilled; 62 g. of the mixed phosphate, b. 62–70° C. at 3 to 4 mm., was obtained.

To obtain the polymer, the 62 g. of distillate was heated to 85–90° C. and 1.2 g. benzoyl peroxide added. After 1 hr. at this temperature, another 1.2 g. benzoyl peroxide was added, and the temperature maintained for 2 hr. more. Pouring the reaction mixture into 400 ml. of petroleum ether precipitated the polymer. After kneading with several changes of petroleum ether, the polymer was dried under vacuum. This polymer, a viscous liquid, analyzed: 10.23% phosphorus, 34.15% carbon, 4.01% hydrogen, and was calculated to contain 30.48% fluorine.

The phosphorus-fluorine polymer was applied to 8-oz. cotton twill from a 25% solution in ethylene chloride–methanol azeotrope. Impregnation with squeeze rolls was followed by oven drying for 30 min. at 110° C. An add-on of 24 to 26% was obtained. This treated fabric was compared with those with similar add-ons of brominated and unhalogenated triallyl phosphate polymers.

The flame resistance of these fabrics could not be compared by the Vertical Flame Test, as all gave good results with little difference in char lengths. Obvious differences, however, were noticed if a vertical edge of the fabric was ignited. Therefore, testing was accomplished by application for 3 to 5 sec. of a small flame to the bottom of a vertically hung ¼-in. strip of fabric [5]. This test served to show the marked difference in the three treatments. Fabric treated with the unhalogenated phosphate polymer burned completely while that treated with the brominated polymer never exhibited more than a momentary afterflame. The fabric treated with fluorinated polymer burned completely, although at a slower rate than that treated with the unhalogenated phosphate polymer.

Phosphorus-iodine polymer. As the preparation of an addition polymer containing iodine was expected to be difficult, a phosphate polyester with

TABLE I. Minimum Add-ons of Inorganic Halides Required to Impart Flame Resistance to 8-oz. Cotton Twill

Halide	Add-on required (% of fabric weight)
Lithium fluoride	Greater than 30
Zinc fluoride	14–17
Magnesium fluoride	Greater than 40
Ammonium chloride	Greater than 24
Lithium chloride	6–7
Zinc chloride	5–6
Magnesium chloride	7–9
Ammonium bromide	5–6
Lithium bromide	5–6
Zinc bromide	7–8
Magnesium bromide	3–4
Ammonium iodide	4–7
Lithium iodide	4–5
Magnesium iodide	5–7

Fabric was considered flame-resistant when a char length of less than ten inches was obtained in the Vertical Flame Test.

iodine-containing groups was made. The preparation and use of this polymer follow.

To 30 g. (0.2 mole) phosphoryl chloride, 40 g. (0.21 mole) 3-iodopropanol was added dropwise with stirring. The reaction mixture was kept below 70° C. and protected from atmospheric moisture. Twelve grams (0.2 mole) ethylene glycol was added slowly with enough ethylene chloride to keep the reaction mixture fluid. After standing overnight, the mixture was shaken with 1% aqueous sodium thiosulfate until the iodine color was removed. Removal of ethylene chloride under vacuum left 40 g. of a gummy product which contained 40.0% iodine and 5.94% phosphorus.

Eight-ounce cotton twill was treated with an ethylene chloride solution of the phosphorus-iodine polymer. Drying was accomplished in 10 min. at 50 to 55° C. The fabric with 22% add-on had 1.6% phosphorus and 9.5% iodine. It showed excellent flame resistance, comparable to the phosphate polymer with the same percent by weight of bromine. Both the brominated and iodinated polymers at 14% add-on failed to prevent burning of the $\frac{1}{4}$-in. strips.

Discussion

The results in Table I show that, of the inorganic halides, bromides and iodides are in general most effective, equally so on a weight basis, and fluorides are the least effective. Contrary to previously reported results [2], it was found that ammonium chloride is ineffective as a flame retardant up to 24% add-on, although fabric so treated burns only slowly, with a small, nearly nonluminous flame. Because of its instability, satisfactory application of ammonium fluoride could not be obtained.

It is interesting to compare the chloride and the fluoride of lithium as flame retardants. Schuyten, Weaver, and Reid [6] have proposed that flame resistance in cotton is obtained by the dehydrating action of a Lewis acid on cellulose. Lithium fluoride would be expected to be a stronger Lewis acid than lithium chloride, and therefore more efficient as a flame retardant. The proponents have pointed out, however, that the charred residue from lithium chloride–treated cotton contains a greater molar quantity of lithium than chlorine, indicating loss of chlorine in the gaseous products. This is confirmed by the alkalinity of an aqueous extract of the char. Char from lithium fluoride–treated cotton, however, yields no alkali even on extended extraction in a Soxhlet extractor. These results suggest that the greater effectiveness of lithium chloride as compared with lithium fluoride is due to free chlorine decreasing the flammability of the gaseous products.

The halogens in the organic phosphorus-halogen polymers show the same order of effectiveness as in the inorganic halides. This result could be expected if the halogen serves as a flame repressant in the volatile products of the cellulose decomposition. Thus the effectiveness increases with decreasing stability of the carbon-halogen bond.

In the fluorine-containing polymer tested, the fluorine is contained in trifluoromethyl groups. It was considered possible that the trifluoromethyl group would be separated as a unit on thermal decomposition and have a flame-retarding action. If this does occur, the flame-retarding action is only very weak.

The poor results obtained with the phosphorus-fluorine polymer, and also the inorganic fluorides, have led to the conclusion that fluorine has little value in flame-retardant agents for cotton.

The phosphorus-iodine polymer gave very good flame resistance, but no better than the phosphorus-bromine polymer at the same add-on. The disadvantages in the use of iodine compounds, namely, their expense and low chemical stability, make them of less practical value in flame retardants. Bromine and chlorine, then, are the halogens that have practical value in flame retardants for cotton. Brominated compounds require lower add-ons, but chlorinated compounds may often find use because they are less expensive.

Summary

The effectiveness of certain inorganic and organic compounds of fluorine and iodine as flame retardants for cotton has been examined. Comparison with other halogenated compounds shows that on an equal weight basis, the order of increasing effectiveness of the halogens is: fluorine, chlorine, bromine, iodine, with the last two about equally effective.

Bromine appears to be the most effective halogen for use in flame retardants for cotton. Although iodine is about equally effective, it has the disadvantages of expense and low chemical stability. On the other hand, chlorine offers advantages in cost that may offset its lower efficiency. Fluorine appears to be almost valueless.

Acknowledgments

The authors are grateful for the assistance of Mrs. A. M. Keller and Mrs. J. P. Evans for the textile testing, and H. P. Pastor, P. J. Murphy, and L. E. Brown for the chemical analyses described in this article. The authors are also indebted to A. J. McQuade of the U.S. Army Quartermaster Corps for his interest and advice in this work.

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Letters to the Editor

Short communications in the form of Letters to the Editor are intended to provide prompt publication of significant new research results and to permit an exchange of views on papers previously published in the JOURNAL. These communications are not submitted to formal review as are research papers, and the editors do not assume any share of the author's responsibility for the information given or the opinions expressed. When work previously published in the JOURNAL is the subject of critical comment, the authors of the original paper are given an opportunity to submit a reply, which will be published concurrently when possible.

The Effect of Solvents on Wool Dyeing

Swedish Institute for Textile Research
Göteborg, Sweden
April 26, 1956

To the Editor
TEXTILE RESEARCH JOURNAL

Dear Sir:

The rate of sorption of many dyes on wool is controlled by the cuticle of the fiber. Lindberg [2] has shown that it is the surface layer of the cuticle which is the main "barrier" for dyestuffs and other polar substances. However, on unmodified wool some parts of the surface layer can be easily penetrated by dyes, resulting in large differences in dyeing rate from fiber to fiber and between different parts of the same fiber. The treatment of wool with alcoholic potash results in an increased dyeing rate, caused by an increased and homogeneous permeability of the surface layer.

By treatment of wool with alcoholic potash or chlorine, the weakly polar and hydrophobic surface becomes hydrophilic and permeable to polar substances, e.g., dyestuffs. This change in character is confirmed by the fact that mineral oil is strongly absorbed to the weakly polar wool surface but can be easily removed from chlorine-treated wool [3].

As was pointed out by Lindberg [2], the whole problem of continuous dyeing of wool is dependent on the possibility of making the permeability of the surface homogeneous, either by treating the fibers or by selecting proper dyes and dye assistants.

Such dye assistants, prepared to increase the dyeing rate, are used for synthetic fibers and are known as "carriers." Although the theory of carrier-dyeing is not fully worked out, the mechanism of carrier dyeing given in Kramer's paper [1] is very interesting. According to this paper the carrier is adsorbed on the fiber surface, and in this layer the dye concentration is higher than in the bath, thus giving rise to a higher concentration gradient, causing a higher diffusion rate in the fiber. The dye is also considered to be disaggregated in the carrier layer. Another effect of the carrier is an opening of interior bonds, e.g., hydrogen bonds, thus facilitating the penetration of the dye. Contrary to synthetic fibers, wool is highly swollen in aqueous dyebaths, and thus the effect of carriers on the surface is probably more interesting in wool dyeing. If the former mechanism of carrier dyeing is used for dyeing wool fibers, this would mean absorbing a carrier substance on the surface.

A year ago Peters (private communication) drew our attention to the fact that addition of butanol to the dye bath increased the dyeing rate of wool. As butanol has a hydrocarbon chain, it seems possible that butanol, like mineral oil, could be absorbed on the surface of the wool fiber and thus act as a carrier under the experimental conditions used. An investigation was made in order to test this hypothesis.

Experiments have been performed on a series of acid dyes differing only in the degree of sulfonation. As the equilibrium exhaustion is about the same for the dyes used and only affected by the alcohols to a small degree at the concentrations used, the time of half-dyeing can be used as a measure of the dyeing rate. At the experimental conditions (wool top cut to pieces of 2 mm. length, high stirring rate, bath ratio 1:250, pH 2.6, and temperature 60° C.) the time of half-dyeing was decreased ten times by the addition of 3% amyl alcohol to the volume of the bath, for the monosulfonated dye (Naphthalene Red JS; CI No. 176). Similar conditions increased the dyeing rate four times for the disulfonated dye (Naphthalene Red EAS; CI No. 182), and the rate was unchanged for the trisulfonated dye (Naphthalene Scarlet 4RS CI No. 185). When determining the partition ratio for the dyes between a water solution and amyl alcohol, the monosulfonated dye was completely absorbed by the alcohol phase, the trisulfonated remained in the water phase, and the disulfonated was soluble in both the alcohol and water (in a partition ratio of 1:4).

Obviously the degree of sulfonation determines the solubility of the dye in the amyl alcohol, and this solubility, at least to some extent, is a necessary condition to get an increased dyeing rate.

However, the new group of wool dyes, known as 1:2 chrom-complex dyes, has been developed to obtain dyes with reduced hydrophilic character, which are still soluble in water, sometimes with the help of dispersing agents [5]. These dyes do not contain any sulfonic acid groups at all, and the effect of amyl alcohol is much greater than on the monosulfonated acid dyes. In Figure 1 are shown some exhaustion-time curves on wool top dyed with Cibalanblau BL. The time of half-dyeing is decreased 100 times at 60° C. by the addition of 3% amyl alcohol to the bath. Dyeing experiments have also been performed on the same wool top, treated with sodium hydroxide in butanol-kerosene, under conditions which make the epicuticle permeable to dyes, but without changing the bulk properties of the fiber. As expected, the dyeing rate is increased, but when these fibers are dyed in the presence of amyl alcohol, the increase in the dyeing rate caused by the alcohol is of a much smaller order of magnitude than with the untreated fibers, where the epicuticle is for the most part intact. Figure 1 shows that the time of half-dyeing only decreases twice

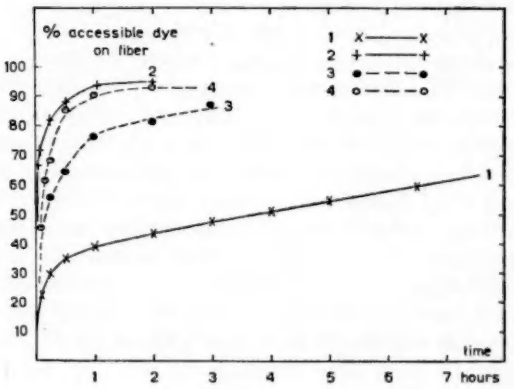

Fig. 1. Dyeing rate of Cibalanblau BL on wool top. (Temperature 60° C., bath ratio 1:250, pH 6.4, dye concentration 0.1 g/liter at $t = 0$. 1, Untreated wool; 2, untreated wool, 3% amyl alcohol in the dye bath (on bath volume); 3, wool treated with sodium hydroxide in butanol-kerosene; 4, wool treated as 3, and 3% amyl alcohol in the dye bath.

(compared to 100 times). This can be explained if we assume the effect of the amyl alcohol mainly to be due to an absorption of the alcohol on the hydrophobic epicuticle. By treatment of the wool with sodium hydroxide in butanol-kerosene, the surface becomes highly hydrophilic, and the absorption of the "hydrophobic" alcohols probably is changed both in degree and kind.

A further support for this theory is obtained if the dye distribution between different fibers and between different parts of the same fiber is studied. For this purpose fiber samples were taken from the dye bath at different times and examined under the microscope. Hundred fibers were classified in four classes: undyed, lightly dyed, heavily dyed, and spot-dyed. For the monosulfonated acid dye, practically all fibers belonged to one class after 2 min. dyeing (lightly dyed) and also after longer times (heavily dyed) in the presence of butanol (5%) or amyl alcohol (3%); whereas without addition of these alcohols, 50% of the fibers were undyed after 2 min., and the rest divided among the three other groups. After 40 min. there were still some spot-dyed fibers, but the main part consisted of lightly and heavily dyed fibers.

Generally, we have found that if the dyeing rate is increased by "hydrophobic" alcohols, the dye distribution becomes more uniform from fiber to fiber and between different parts of the same fiber. This indicates that through the absorption of alcohols, the epicuticle becomes almost homogeneously permeable to those dyes which are soluble in the alcohols.

Examination of the cross sections of the wool fibers after dyeing reveals some interesting facts. If the dyeing is performed on wool top with Cibalanblau BL at 60° C. and a bath ratio of 1:250 at pH 6.4, the bath will be exhausted to 90% after 30 min. and to 95% after 2 hr. in the presence of 3% amyl alcohol. After dyeing 2 hr., practically all fibers are penetrated by the dye. Without amyl alcohol an exhaustion of the bath of 95% is not obtained until 3 days have passed and then 95% of the fibers are still ring-dyed. It is thus highly probable that the dye is molecularly dispersed in the layer consisting of alcohol-wool surface. In water solution however, the 1:2 chrom-complex dyes are highly aggregated, and the addition of amyl alcohol or butanol will make the dye molecules still more aggregated in the solution, as can be seen from the increased tendency for the dye to precipitate.

An increased dyeing rate has been obtained with many alcohols, partly soluble in water, whereas the lower, completely soluble alcohols have only a very small influence on the dyeing rate. Although we have investigated the effect of alcohols, other organic substances may also be effective in increasing the dyeing rate of wool. Stevens and Peters [6] report this to be the case also for sparingly soluble amines and phenols, and they have examined the effect of thymol in more detail.

The possibility of using the mechanism of "carrier" dyeing for wool with simple organic substances as carriers is of great practical importance. The possibility of dyeing at low temperature has already been stressed by Peters and Stevens [4]. However, the time of dyeing at 100° C. can be made short enough to make continuous dyeing processes very promising. For this purpose the increase in the fiber-to-fiber levelness is very important.

As the effect is greater when the hydrophilic character of the dye is reduced, there are great possibilities for the dye manufacturers to modify their dyestuffs to be more suitable for water-solvent dyeing.

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MARIANNE KÄRRHOLM
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INDUSTRIAL SECTION

The Loom-Action-Type Abrader

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THE process of weaving yarn into fabric is such that the yarn is subjected to abrasive and tensile actions. These often cause some yarn ends to break, resulting in expensive loom stoppages. In the attempt to prevent or at least minimize this yarn breakage, sizing compounds are applied to the yarn. It thus becomes necessary to evaluate objectively the effectiveness of each new batch of sizing.

Several types of abraders have been developed in the past. This paper reports a warp yarn abrader which incorporates as nearly as practical the abrasive-tensile actions of the actual loom operation. Tests conducted proved its exactitude and value.

Introduction

No method has been adopted as yet as a standard for determining the effectiveness of a sizing compound on the weavability of a yarn. The most positive way of accomplishing this task is to undertake full-scale loom operations. Obviously this is not particularly acceptable because it is expensive in time and effort. Many devices and techniques have been proposed as solutions to this problem. However, because of disadvantages ascribed to each, none are as yet widely accepted. The present development, herein described, resulted in an apparatus which very nearly emulates the loom actions that affect the warp yarn functionally as well as quantitatively.

TABLE I. Breakage Causes

Warp breakage	Per cent of all breaks
Attributed to sizing	24.7
Not attributed to sizing	41.5
Unknown	33.8

It is agreed that the weaving properties of yarn are influenced by factors other than sizing formulas. A study by Brown [1], for instance, gave rise to a classification of the nature and incidence of warp breakage, as shown in Table I.

Although 15% of the 33.8% is definitely established as of unknown origin, a good portion of the remaining 18.8% can be attributed to sizing, either directly or indirectly. Consequently as much as 40% of all yarn breaks could be assigned to sizing compounds. Ideal formulas could thus theoretically eliminate 40% of the yarn or end breaks. To develop such formulas an effective abrader is needed; one that will rapidly and accurately assess the great number of formulas that must be tried. The loom-action abrader is not claimed to be the final answer; nevertheless, preliminary test results [4] are indicative of its potentialities.

Prior to the design of the loom-action abrader, an investigation of every abrasive and tensile action of any consequence was carried out on a standard weaving loom [3]. The results, as obtained, were carefully scrutinized and those which appeared well founded were employed in the quantitative design of the abrader. The actions studied involved the tension variations on a single end for a complete harness cycle as well as the frictional effects at all locations where either longitudinal or lateral rubbing existed. This included the lateral rubbing of warps occurring when the two harnesses pass the closed-shed position. The theory associated with these frictional determinations was based on the fundamental principles of work and energy (see Appendix A).

The Loom-Action Abrader

The line diagrams of Figures 1 and 2 portray the similarity of action between the loom-action abrader

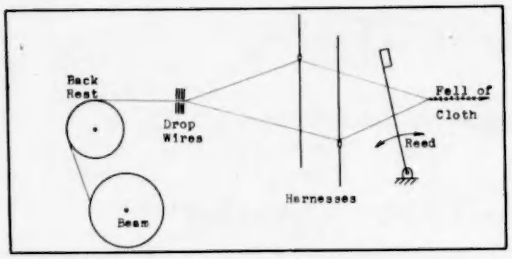

Fig. 1. Cross section of actual loom.

and an actual loom. For rapidity of testing, a simplified threading technique was devised for the abrader. A single end of yarn is trained over and under pins and rollers following the path shown in Figure 2. Each yarn must be sufficiently long to permit three complete threading cycles. Thus the device abrades the equivalent of six ends for each setup.

To follow the ensuing explanation of an operating cycle of the abrader, refer to Figure 2. Position 1 shows the harness in the open-shed phase. In position 2 the harnesses have been partly displaced, one upward, the other downward, and the eccentric has swung counterclockwise to take up the slack resulting from the movable pins. In position 3 the harnesses become level and both the movable pins and the eccentric have assumed their maximum rotation. The harnesses then dwell for an instant while the reed performs its function of beating the weft. The second half of the harness cycle is a reverse repetition of that described. In addition, however, a pawl and ratched arrangement concomitantly releases and draws the warp through the tension rolls at a rate

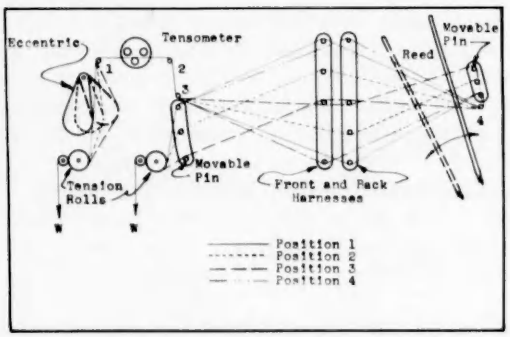

Fig. 2. Laboratory abrader with harnesses in four positions. Note: Pins 1 through 4 are fixed. *W* indicates equal hanging weights.

of 1 in./45 picks. This action repeats itself at a speed of 155 cycles/min. In essence the loom-action abrader is a miniature loom without a shuttle action.

Testing Procedure

The experimental procedure entailed in evaluating the abrader consisted of testing numerous ends of sized yarn (cotton 22's). The tests were conducted using the K. Zweigle abrader [2] and the loom-action abrader and the results compared. Light, medium, and heavy sizing compounds were used. A record of the number of harness cycles required to break each sample end was kept. In addition, a number of tensile strength tests were performed.

Using the data from the abrader, standard deviations and cumulative frequencies were determined.

Results

The results enumerated in Table II clearly indicate that such static tests as per cent elongation and tensile strength are insufficiently sensitive to sizing changes to warrant their use in assessing the weaving qualities of a sized warp. The resistance to abrasion on the other hand does appear quite sensitive to sizing changes. Therefore indications are that loom-action abrader results could be used as sufficient criteria for arriving at adequate indices of weavability.

The figures given for the standard deviation percentage of the K. Zweigle results depict a wide dispersion on either side of the mean. However, a narrow and considerably regular distribution is noted for the data obtained with the loom-action abrader. It is obvious that if a combined stress-abrasion tester is to be reliable in evaluating sizing compounds, it must closely reproduce the action which a warp yarn

TABLE II. Summary of Test Data by Two Abraders

Mat.	Abrader	Mean no. of cycles to breakage	Std. dev. from mean (%)	Avg. tens. strength (g.)	% Elong.
Light	Zweigle	107	51.4	360	4.9
	Loom-action	554	13.5		
Medium	Zweigle	163	34.4	340	4.8
	Loom-action	651	9.2		
Heavy	Zweigle	205	38.6	345	4.6
	Loom-action	762	15.4		

will normally undergo in the weaving loom. The loom-action abrader does this reasonably well. Its salient and important characteristic is therefore exactitude. It appears then that the full development of this abrader should provide a valuable addition to textile testing equipment.

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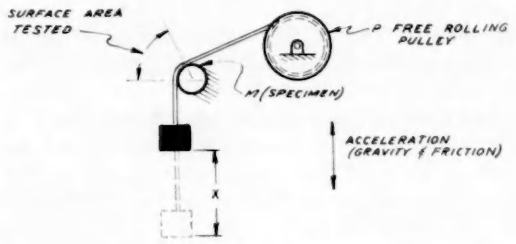
Appendix A



To determine the dynamic friction exerted by the surface being tested:

By the principle of work and energy. . . .

The total potential energy lost by the system is equal to the total kinetic energy gained by the system plus frictional losses, during the time interval that the weight drops a distance

$$\sum \text{P.E.} = \sum \text{K.E.} + \text{frictional losses}$$

$$Wh = \tfrac{1}{2}mv_W^2 + \tfrac{1}{2}IW_P^2 + f_M + f_P \qquad (1)$$

If the initial velocity of W is zero and the accelerations (gravitational and frictional) are constant, then

$$S = V_{\text{a.v.g.}}t = \frac{V_{\text{final}}}{2}(t) \qquad (2)$$

or

$$V_{\text{final}} = \frac{2S}{t} \qquad (3)$$

also

$$W = \frac{V}{R} = \frac{2S}{tR} \qquad (4)$$

In Equation 1, such terms as V_W and W_P are unknown but can be substituted by Equations 3 and 4. This converts Equation 1 into terms which are readily measured. Although the only two terms unknown in the equation are f_M and f_P, an independent run, involving the free rolling pulley only, would yield its dynamic frictional resistance of f_P. Thus, f_M which is the value being sought, becomes the only unknown in the equation.

Manuscript received December 15, 1955.

National Cotton Council of America

Seventh Cotton Research Clinic

The papers in this issue comprise those given at the Seventh Cotton Research Clinic of the National Cotton Council of America, held in Pinehurst, N. C., February 15–17, 1956. Other papers presented at the Clinic appeared in the May issue. Reprints of the entire proceedings, bound in a cover, will be distributed through the Cotton Council upon completion of the series.

Comparative Quality Characteristics of Selected Growths of Cotton in the 1955 Crop

J. M. Cook[1]

Agricultural Marketing Service, U. S. Department of Agriculture, Clemson, S. C.

Introduction

Each fall there is a "rush" by cotton merchants and mill men to get all available information on the quality of the new crop. Through various channels they obtain this information and plan their purchases accordingly. When the first samples from the early crop are of poor quality, an effort will be made to keep a supply of old cotton on hand and the buying of new cotton will be postponed until later in the season, with the hope that the midseason and late parts of the crop will be better than the first. At the same time, samples from other areas of the Cotton Belt will be tested to determine if the cotton is suitable for their needs, for we know that one area may produce below average cotton, while another, not so far away, will be much better in quality.

This difference in quality of cotton grown in one section as compared with that from another gives the cotton buyer a real problem, since he would like to obtain, in most cases, as even-running lots as possible for his customers or mill, and at the same time at as low a price as he can. It has been very influential in encouraging buying according to the general area in which cotton is grown, such as "Delta," "Eastern," "Texas," or "California." These terms bring to the mind of the average mill man relative qualities equally as pertinent as fiber properties, such as "fineness" or "strength."

These differences in quality also present problems after the cotton has been delivered to the mill because not only are there variations from area to area, but also within one area as well, and the mill desires the day-to-day mixes as high in quality and as uniform in quality as the available supply will allow. When the product drops below the standard in quality, such as strength, appearance, or running quality, a change must be made.

Instruments for measuring the fiber properties of cotton have been developed and become available to the trade over the past few years. It is possible through their use to hold day-to-day mixes fairly uniform. The testing of bale samples for length, length uniformity, strength, fineness, and maturity, according to area in which they are grown, and the proper application of these data will aid in holding mixes at the level of quality desired.

Samples and Test Data

The Cotton Division of the Agricultural Marketing Service, U.S. Department of Agriculture, has been making fiber and spinning tests during the past ten years on samples from cotton-growing areas across

[1] In charge of Clemson Cotton Laboratory, Cotton Division.

the Belt. Spinning test lots consisting of from 15 to 35 bale samples are collected by the classing offices to represent a particular period of harvesting from each gin point represented. The samples selected are of the predominating grade and staple received from producers organized for cotton improvement. Early, midseason, and late harvested samples each are composited to represent the particular part of the season. The data from these tests are published monthly as the cotton is harvested, and then a summary report for the whole season is published after samples from all areas are tested.[1] Thus, one may obtain from a study of the results of these reports comparisons of the time of harvesting, location of growths, varieties, and seasonal conditions.

Cottons representing the most popular varieties grown in the United States, and thus most of the staple lengths produced, are included in the study. The bulk of the cottons grown, however, are from varieties bred to produce staple lengths of $1\frac{1}{32}$ to $1\frac{3}{32}$ in. Because of this, those varieties producing cotton in this staple length range were selected for this paper.[1] In some locations the average staple for a particular lot was shorter than $1\frac{1}{32}$ in.; however, the lot was included since it was from one of the selected varieties.

The fiber tests made on each spinning test lot are as follows:

Fiber length by Fibrograph
Fiber fineness and maturity by Causticaire method
Pressley strength
Shirley Analyzer nonlint content
Soluble sugar content
Color measurements

Spinning test data obtained include

Manufacturing waste
Neps in card web
Yarn strength
Yarn appearance

Bleaching and dyeing tests were also carried out on all spinning lots, and mercerizing data were obtained for lots from which combed yarns were spun. The data on the finishing tests are not included in this paper.

Each lot of cotton included in this study was spun into carded 22's and 50's counts of yarn. Standard laboratory techniques and procedures were used in all of these tests so that the results from one sample of cotton are comparable with any other.

In this study, the results from all lots of the selected varieties from each state and time of harvesting were averaged for the particular spinning criteria of quality and fiber property. In some states more than one variety was represented. In all areas, the seasonal conditions varied from place to place and, doubtless, had an influence on the results. The average from a particular state, however, is probably more in line with a mill mix than could be obtained from a single gin point.

Yarn Strength

Figure 1 shows graphically the average break factor for the two counts of yarn spun from the samples of each state according to the time of harvesting.

In all states except Arizona the early cottons produced the strongest yarns. This was followed by the midseason lots, with the late samples yielding the weakest yarns. Those from Arizona were in reverse order, with the late samples giving the strongest, the midseason the second, and the early the weakest.

The cottons from 3 states, namely, North Carolina, South Carolina, and Arkansas, produced yarns that showed a difference in average strengths of 10% or more between the early and late season harvestings. Those from 6 states showed a difference of between 5 and 10%. These were Tennessee, Mississippi, Missouri, Louisiana, Texas, and Arizona, with the weakest cotton from Arizona coming from the first picking. Cottons from the other 3 of the 12 states reflected less than 5% difference between the first and late season pickings. It should be noted that each of these gave differences greater than 3%, which is considered significant.

The level of quality of yarn, as reflected by strength, varied over a wide range—from 1880 as the average for the late cotton from North Carolina, to 2532 for the early cotton from California, a difference of more than 34%.

The cottons producing the strongest yarns were from California with break factors ranging from 2532 for the early cotton to 2443 for the late. The yarns from the Alabama-grown cottons were about 4% lower—ranging from 2435 to 2355. These were followed closely by those from Georgia and Tennessee

[1] Fiber and Spinning Test Results for Some Varieties of Cotton Grown by Selected Cotton Improvement Groups, Crop of 1955. AMS-66 and Supplements 1 to 5.

at less than 2% lower level. The weakest yarns were spun from the North Carolina cottons with break factors ranging from 2072 to 1880.

Cottons from 3 states reflected much greater differences between the early and midseason samples than between the midseason and late season. This is true with the Mississippi, Missouri, and Arkansas cottons. In these 3 states the yarns from early samples were more than 5% stronger than the midseason.

From these results it is apparent that there was a significant difference in the quality of the early and midseason cottons, and midseason and late samples for strength of yarn, with the later cottons reflecting the lower strengths.

It is interesting to note these data, which are averages, and estimate the difficulty of obtaining mill mixes that are even-running from the standpoint of yarn strength. The necessity of using a mix representing several shipping points may readily be seen if one is to retain a fairly uniform mix from day to day.

Yarn Appearance

Figure 2 shows graphically the average yarn appearance index for the two counts spun from the lots of cotton according to state and time of harvesting. (A C+ grade is considered an index of 100; an index of 90 equals C, and one of 110 equals B.)

The early and midseason samples were not consistent in their quality for producing smooth yarns.

Note that the early season gave slightly higher grades than the midseason from 5 states, while the midseason from 3 states gave higher grades than the early, and the grades from the early and midseason were the same in 4 states.

The late cottons produced the lowest yarn grades of the 3 harvestings from 11 out of the 12 states. This proportion is the same as that indicated by the yarn strengths.

The average from each harvesting period for Alabama was at the same level, namely, between the C+ and B grades.

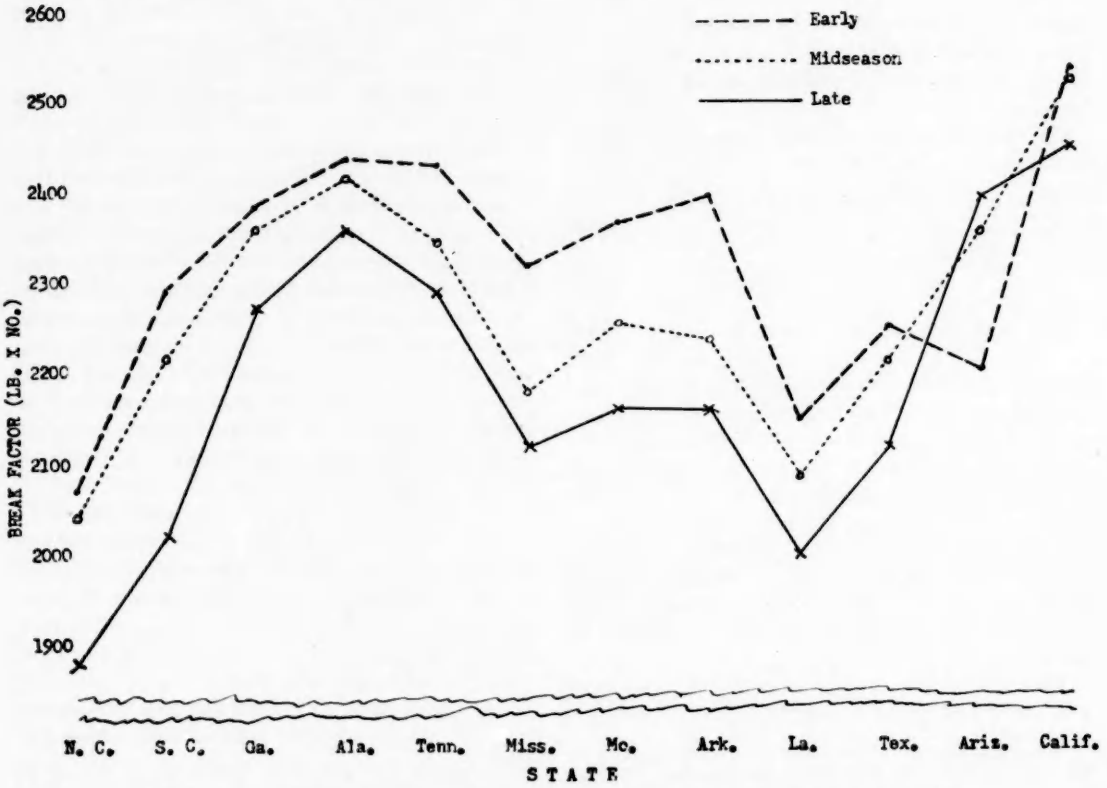


Fig. 1. Average break factor for yarns spun from 1955 cottons, by state and time of harvesting.

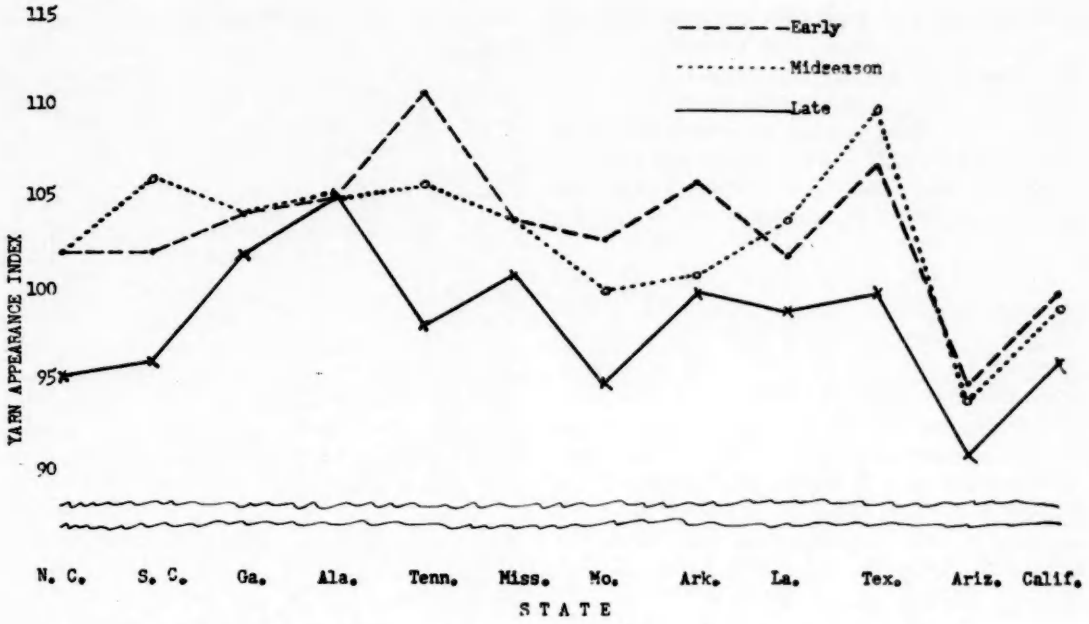


Fig. 2. Average yarn appearance for yarns spun from 1955 cottons, by state and time of harvesting.

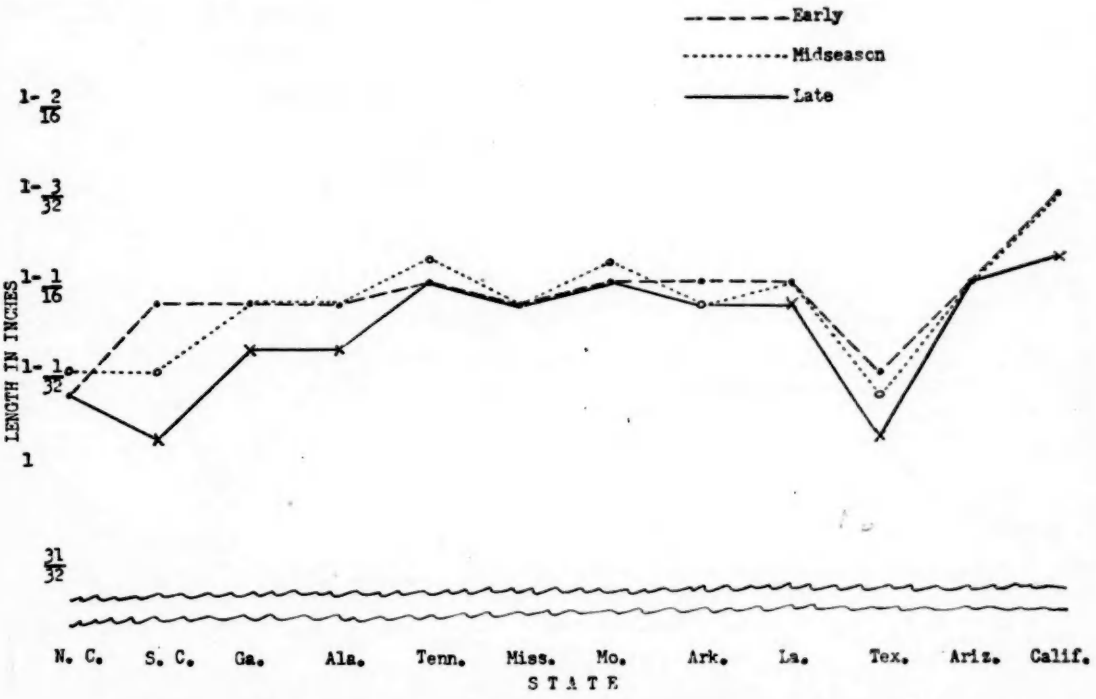


Fig. 3. Average length of 1955 cottons as shown by classification tests, by state and time of harvesting.

The highest yarn grades for all states were produced by the early samples from Tennessee. (It will be remembered that these samples also produced next to the strongest yarns of any of the rain-grown areas.) The next highest were from the early samples from Texas. If we average the early and midseason results from each of these 2 states, the levels are about the same, at index 108, or almost a B yarn.

The yarns of lowest appearance grades were from the Arizona samples, with the next to lowest from California. The average of early and midseason from Arizona was 94.5, between a C and C+ grade, while that from California was 99.5, or a C+.

It is apparent that the late season cottons, on the average, were not as good as the early and midseason for producing yarns of high appearance grade. Let us look at the fiber properties of these cottons and see if we can detect something that could be used as a guide in making the selection of cotton more reliable for obtaining desired end results.

Fiber Properties

Length

Figures 3 and 4 show graphically the average classer's staple lengths and Fibrograph lengths for cottons of this study according to state and time of harvesting.

The staple lengths as given by the classers did not show a consistent difference between the early and midseason samples. Notice that 3 of the early season samples were slightly longer than the midseason—those from South Carolina, Arkansas, and Texas—and 3 of the midseason slightly longer than the early season, namely, North Carolina, Tennessee, and Missouri. The averages from 6 states showed the early and midseason the same length. In 2 states the averages from all 3 harvestings were at the same level, namely, Mississippi and Arizona.

The late season samples from 6 out of the 12 states averaged shorter in staple than either the early or midseason samples. Although these differences are small, they indicate that the classers probably

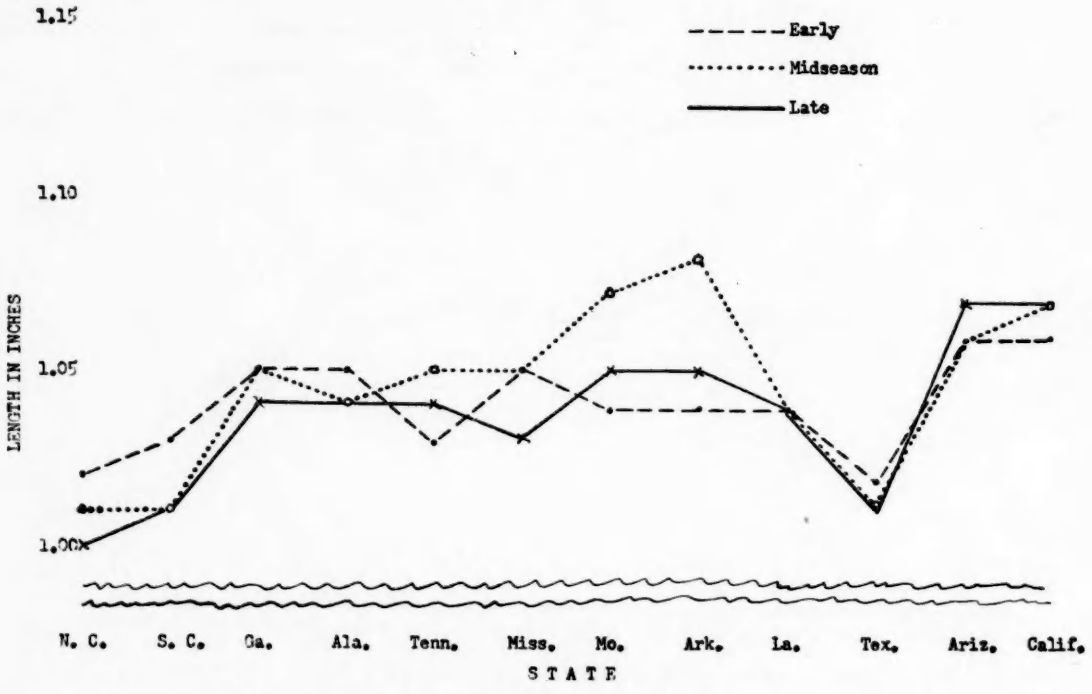


Fig. 4. Average length of 1955 cottons as shown by Fibrograph tests, by state and time of harvesting.

detected a difference in the cotton from the late harvestings, since the number of bales on which these points were based ranged from approximately 80 to several hundred. There was no sample of the late cottons that averaged longer than either the mid- or early season.

The samples from California averaged the longest at slightly less than $1\frac{3}{32}$ in. The averages for the Tennessee, Missouri, Louisiana, and Arizona were at approximately the same level, namely, $1\frac{1}{16}$ in. Those from North Carolina and Texas averaged the shortest at slightly less than $1\frac{1}{32}$ in.

The Fibrograph results showed that the samples of the midseason from 3 states were slightly longer than either the early or late season samples. The other samples did not reflect as great a difference except for one case, namely, the early season from South Carolina averaged 0.02 in. longer than either the mid- or late season. Three of the averages for early season showed longest; three of the midseason were longest and one of the late season. Three of the early season averaged shortest, 2 of the late season averaged shortest, and none of the midseason were shortest.

The midseason samples from Arkansas were the longest of any, and the midseason from Missouri were at the same level as the longest from Arizona and California, namely, 1.07 in. Those from Georgia, Alabama, Tennessee, Mississippi, and Louisiana averaged about the same length, when all 3 pickings are considered. The shortest were from North Carolina, South Carolina, and Texas at between 1.01 and 1.02 in.

These results indicate that the classer detected more of the poorest spinning lots and expressed this by calling the staple slightly shorter than the others.

Fineness and Maturity

The average fiber fineness data according to time of harvesting are shown graphically in Figure 5, while the maturity data are shown in Figure 6.

There were 4 states from which the samples of the early harvesting averaged 0.2 μg./in. or more coarser than those of the second picking. These were

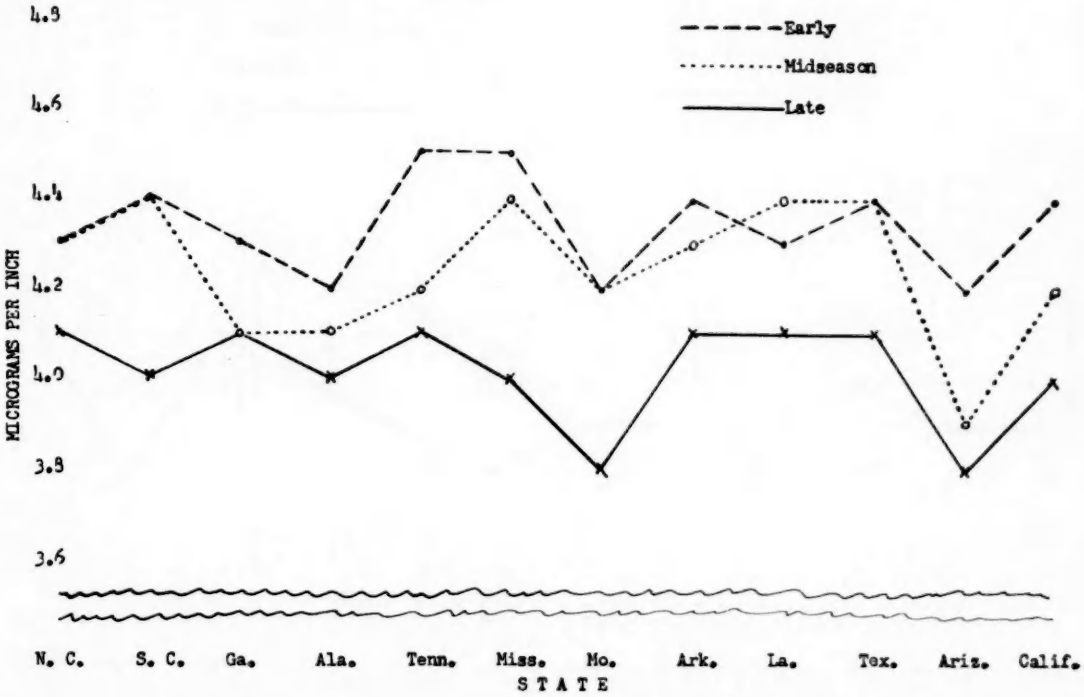


Fig. 5. Average fiber fineness in micrograms of 1955 cottons by state and time of harvesting.

Georgia, Tennessee, Arizona, and California. One of these 4 showed 3% difference in maturity, and for this the early sample was slightly more mature. Thus, the difference in fineness between the early and midseason samples shown by these states was, doubtless, due to a coarser fiber for the early cotton rather than high maturity of fiber.

The results from 11 states indicated the late season samples as being finer than either the early or midseason. These differences ranged from 0.1 μg./in. (3 states) to 0.4 μg./in. In all cases, with the possible exception of Arizona, the maturity should have had only a negligible effect on these differences in fineness. The fiber maturity measurements showed the early season samples more mature from 8 out of the 12 states.

Strength

Figure 7 shows in chart form the average fiber strengths in 1,000 lb./sq. in. using 0 gauge between the Pressley clamps for each state and time of harvesting.

The results from 5 out of the 12 states gave strengths in order of strong to weak as early, midseason, and late samples, or in the same order as the yarn strength results. These states were North Carolina, South Carolina, Missouri, Texas, and California.

The results on samples from 2 of the states showed large differences in yarn strengths between the early and midseason, namely, Mississippi and Arkansas. The fiber samples of the Mississippi cottons broke at 78,000, 77,000, and 78,000 for the early, midseason, and late, respectively. The Arkansas samples broke at 82,000, 80,000, and 80,000, respectively, for the 3 pickings. These differences would not be significant in influencing yarn strengths.

The Louisiana samples gave yarn strengths that were 7.5% stronger for the early season than the late, yet the fiber strength was slightly stronger for the late than the early.

The Arizona samples from the mid- and late season crop were slightly stronger than the late season from California; yet the late season samples from California gave stronger yarns than either.

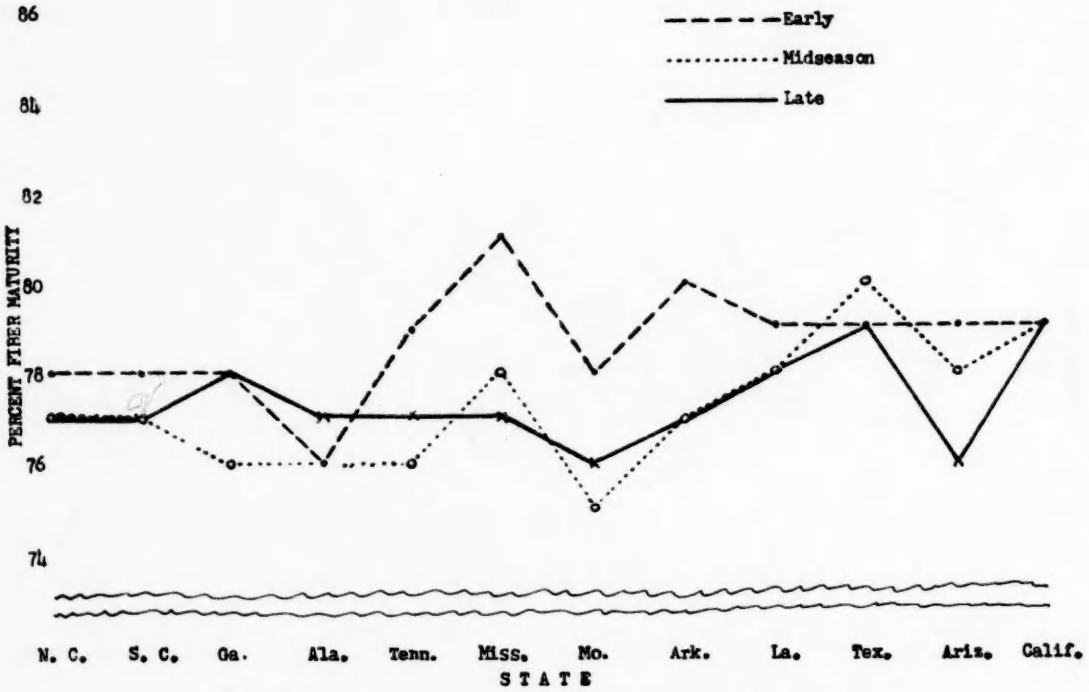


Fig. 6. Average percentage fiber maturity as determined by Causticaire method for 1955 cottons, by state and time of harvesting.

The Mississippi samples were at about the same level of strength as the Georgia and Alabama samples; however, they produced weaker yarns than either.

Referring to Figure 8, the fiber strength results as an index when using a $\frac{1}{8}$-in. spacing between clamps, it may be seen that samples from 5 states gave strengths in the same order as the yarn strengths. (The index may be calculated by dividing 3.19 into the strength-weight ratio and multiplying by 100. The 3.19 is the average ratio for the cottons tested from the 1954 crop.) The 5 states were North Carolina, South Carolina, Georgia, Texas, and California.

The early and midseason samples from Arkansas broke at the same level, with an index of 103.

Although the strengths for the early and midseason samples were not consistent, in that those from some states reflected stronger fiber for the early and others for the midseason cottons, it should be noted that the samples from late season in 9 out of the 12 states averaged weaker than the early or midseason. They were lower than either the early or midseason by 2 or more in 7 out of the 12 states. Probably this is more nearly in line with actual yarn strength results than any other fiber test results.

The coefficient of correlation of these results and yarn break factor is 0.62 as compared with 0.55 for the results from 0-gauge strengths.

It appears that the fiber strength of the cotton for this year is not as significant in estimating probable yarn strength as it has been on many previous crops.

Summary

Fiber and spinning test data on commercially grown varieties that were bred to produce staple lengths of $1\frac{1}{32}$ to $1\frac{3}{32}$ in. are included in this study. Results from early, mid-, and late season harvestings are represented and each is averaged according to the state in which the cotton was grown.

The yarn strength data indicated that the quality of the cotton fell off in all states except Arizona as the season progressed. The early season samples gave stronger yarns, on the average, than the midseason, and the midseason gave stronger yarns than the late season. This order was reversed for the Arizona samples.

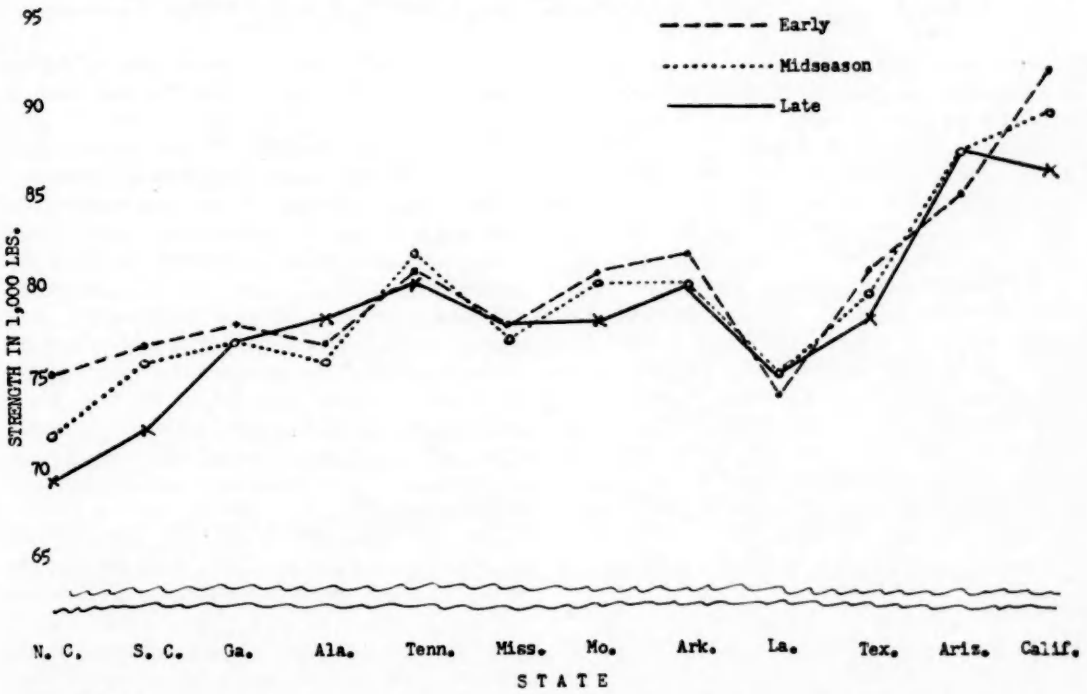


Fig. 7. Average fiber strength by Pressley tests using 0 gauge between clamps, by state and time of harvesting.

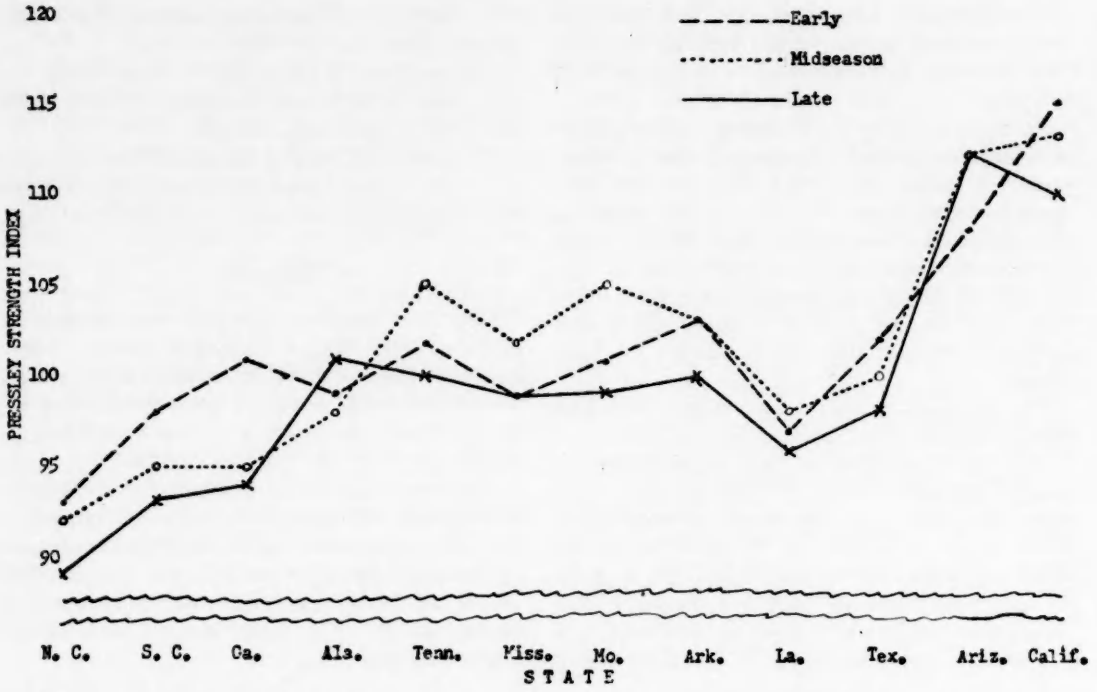


Fig. 8. Average strength by Pressley tests using a $\frac{1}{8}$-in. spacing between clamps, by state and time of harvesting.

The average yarn appearance grades for the early and midseason samples did not reflect a consistent difference in favor of either period of harvesting. The samples from the late picking in 11 out of the 12 states were manufactured into yarns giving the poorest appearance. In some cases the grades were only slightly lower than the early or midseason, but in most comparisons the differences were significant.

The average classer's lengths for the samples of each harvesting period of all states indicated that there were no consistent differences between the lengths of the early and midseason samples. Some comparisons showed slightly longer staple for the early cottons; however, there were 6 states that showed the first and second pickings as the same length. The late season samples in 6 out of the 12 states were called slightly shorter, on the average, than either the early or midseason, which indicates that the classer may have detected a difference in quality.

The Fibrograph results did not reflect enough difference between the 3 harvestings to account for the differences in yarn strengths.

The late samples from 11 out of the 12 states were slightly finer fibered than either the early or late cottons. Seven of the early season periods showed slightly coarser fiber than either the midseason or late.

The fiber from the early samples in 8 of the 12 states was slightly more mature than the midseason or late. These differences varied from 1 to 3% and normally would not be considered significant. There was no consistent difference between the other harvestings.

Only in 3 states did fiber strength results using 0 gauge between clamps show enough differences between the early and late samples to lead one to expect lower yarn strengths from the late cottons. These were North Carolina, South Carolina, and California, although there were averages from 5 states that showed the same trend from early through midseason to late.

Only in 2 states did the strengths obtained from the Pressley tests, using a $\frac{1}{8}$-in. spacing between the clamps, show enough difference between the early and late season cottons to account for the difference in yarn strengths. Generally speaking, most of the differences shown were too small for one to consider highly significant for a particular state when selecting cottons for a mix.

Cotton Quality and Fiber Properties

Part V: Effects of Fiber Fineness[1]

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Abstract

The purpose of this research was to evaluate fiber fineness as a cotton quality factor, especially with regard to processing characteristics and fabric performance. Three lots of cotton having Micronaire values of 3.6, 4.5, and 5.4 were studied. In addition, equal weights of the 3.6 and 5.4 cottons were mixed to prepare a fourth lot of medium fineness to compare with the 4.5 cotton. The cottons were spun into 30/1 yarns, woven into a 66×68 fabric construction, and bleached, mercerized, dyed, and resin-finished. Samples taken throughout the trial were used to determine the properties of the single fibers, rovings, yarns, and fabrics.

Increasing fineness, or decreasing Micronaire, was found to increase roving and yarn strengths, and to decrease spinning end-breakage rates. Maximum yarn strength was reached at lower twists for the finer cottons. Neps increased with increasing fineness.

The fabrics of the finest cotton possessed more strength, more abrasion resistance, more elasticity, and a softer hand than the fabrics of the coarser cottons. Resin treatment eliminated most of the fabric advantages of the finer cottons. Increasing fineness also caused greater fabric shrinkage and somewhat poorer crease recovery. The blended lot was generally equal to the lot of medium fineness in both processing characteristics and fabric quality.

In general these observations suggest that distinct benefits can be obtained by the use of finer cottons, provided the accompanying increase in neps can be tolerated.

Introduction

Cotton breeding programs and cotton selections by fabric manufacturers generally have not taken into account the possible relation between cotton fiber properties and fabric performance. One reason for this failure is the dearth of factual information available on this subject. While certain broad relationships have been established for man-made fibers, it is questionable if these can be applied to cotton. With cotton the ranges of available fiber properties with different varieties are relatively narrow, possibly too narrow to produce fabric effects greater than those produced by changes in construction or finishing treatments. Clearly, experimental work on this problem is needed to provide a factual basis for cotton fiber research, for the development of instruments for testing cotton quality, for the guidance of breeding programs, and for the aid of manufacturers in selecting cottons most suitable for their processing organization and product.

One important reason for the dearth of information on the relationship between cotton fiber properties and the properties of the finished fabric is the relatively high cost of this type of research. The evaluation of the field properties and the processing characteristics of a cotton involves difficulties and expense which increase manyfold if the evaluation is to include the properties of the finished fabric. This situation is further complicated by the fact that there are many fiber properties which may affect fabric quality and that only a few properties can be studied at one time. Subjects for study include not only the conventional bulk fiber measurements but also now

[1] This work was performed as part of the Cotton Research Project of Textile Research Institute and supported by the following member companies: The American Thread Co., Anderson Clayton and Co., Bates Manufacturing Co., Coats and Clark, Inc., Cone Mills Corp., Dan River Mills, Deering Milliken Research Trust, Fabric Research Lab., Inc., Harris Research Lab., Joanna Cotton Mills Co., Johnson and Johnson, Pepperell Manufacturing Co., Standard Chemical Products, Inc., J. P. Stevens and Co., Inc., West Point Manufacturing Co., U.S. Rubber Co., U.S. Testing Co., Inc.

the single-fiber properties [17], such as fiber breaking load, elongation to break, Hookean slope, energy to uncrimp, energy to break, elastic modulus, and breaking stress. The question naturally arises as to which of these properties should be studied first.

In recognition of the fact that it would be of value to clarify the relationship between fiber properties and fabric properties, Textile Research Institute undertook the present study of one recognized, important fiber property—fiber fineness. The objective in this work was to determine the effect of fiber fineness on the properties of the finished fabric as well as on processing characteristics.

The first requirement of the test was the location of a series of cottons which differed only in fineness. After the cottons were acquired and thoroughly checked for fiber properties, they were processed into yarns and finished fabrics under closely controlled conditions. The processing characteristics and fabric properties were then related to the fiber fineness of the cottons.

The Samples

Previous work has revealed that many other fiber properties are closely related to fineness [15]. It therefore was important to obtain a series of cotton samples of the same variety such that insofar as possible there would be no differences except in average fiber fineness. Accordingly, three 3-bale lots of Deltapine 15 were selected from the production of a single Mississippi delta plantation. In addition to a common staple length of $\frac{15}{16}$ in., all the bales were alike in grade and Pressley strength. They differed only in fineness, the three lots having Micronaire values of 3.6, 4.5, and 5.4.

The bales of each type were blended in an opening line and rebaled for future testing and use. The cottons were identified by the code words "Fine," "Medium," and "Coarse." In addition, equal weights of Fine and Coarse were mixed to make a "Blend" lot which was to be compared with the Medium.

Fiber arrays were prepared from bale samples of the original cottons. The results of tests on the arrays for maturity, fineness, and length appear with other test data in Table I.

A comparison of the group-fiber properties indicated that the fineness difference was primarily one of differing maturity. It is interesting to note that the Fine cotton was a little shorter in mean length than the other two. This difference was confirmed by the single-fiber length distribution [16] which showed that the Fine contained more short and fewer long fibers than the Coarse. The number per cent of fibers 0.4 in. or shorter for the three cottons is as follows: Coarse 30%, Medium 33%, Fine 43%. This observation might have been expected, since the Fine fibers would undoubtedly be more easily broken in ginning than would the Coarse ones. The number-length histograms appear in Figure 1.

Because the single-fiber properties of cottons over different varieties have been found to be closely related to fineness and interrelated with each other [15], and in order to ensure that fiber fineness alone would be the cause of any difference in fabric prop-

TABLE I. Bulk Fiber Properties

	Coarse	Medium	Fine	Blend	Methods reference
Maturity					
Array method, %	87	82	74	—	D 1442–54 [3]
NaOH method, %	84.1	62.3	64.3	—	D 1443–53T [3]
Causticaire maturity index	83.5	76.9	73.1	—	[1]
Fineness, μg./in.					
Array	5.3	4.4	3.6	—	D 1442–54 [3]
Micronaire	5.5	4.5	3.6	4.3	D 1448–54T [3]
Strength					
Pressley index					
0 mm.	6.46	6.19	6.72	6.58	[14]
3 mm.	2.41	2.30	2.34	2.21	[14]
Fiber Length					
Array, mean, in.	0.87	0.87	0.84	—	D 1440–55 [3]
Upper quartile, in.	1.04	1.07	1.06	—	D 1440–55 [3]
Coef. of variation, %	28	32	35	—	D 1440–55 [3]
Single-fiber mean, in.	0.64	0.64	0.59	—	[16]

erties, the single-fiber mechanical properties were also determined for each of the original cottons. Ninety-six randomly selected fibers from suitably blended bale samples of each cotton were tested on the Instron Tensile Tester equipped with vibroscope [11, 17]. The results appear in Table II.

In addition to the fiber cross-sectional area, the cottons were found to differ in breaking load and Hookean slope. However, for those properties in which fiber size has been taken into account—namely, breaking stress, elastic modulus, and crimp per unit volume—the cottons are remarkably similar. The samples therefore represent a series of cottons in which the effects of fineness alone can be studied.

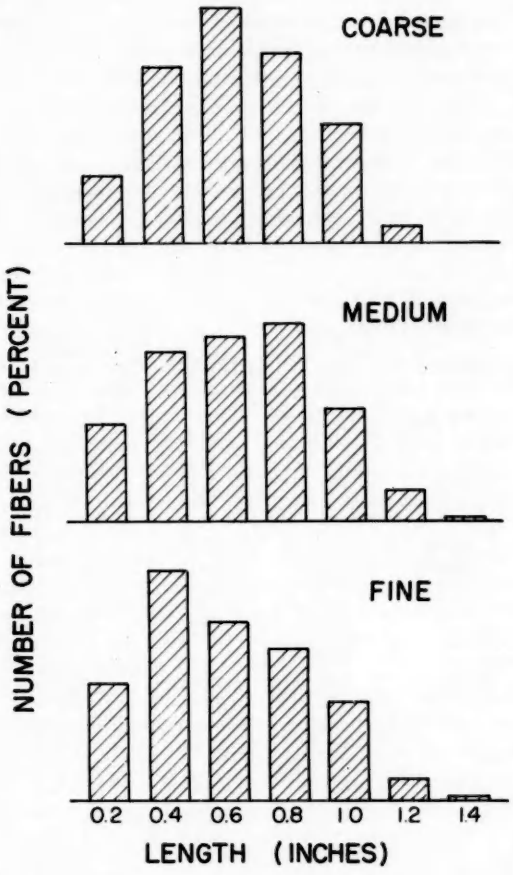

Fig. 1. Number-length distributions obtained from single-fiber length measurements on more than 570 fibers from bale samples of each cotton.

TABLE II. Single-Fiber Mechanical Properties

Property	Units	Coarse	Medium	Fine
Area	$\times 10^{-6}$ cm.^{2}	1.48	1.35	1.17
Breaking load	g.	4.95	4.14	3.92
Breaking elongation	%	7.18	7.07	6.97
Hookean slope	g./1%	0.679	0.563	0.525
Crimp energy	$\times 10^{-3}$ g. cm./cm.	2.94	3.07	2.54
Elastic modulus	$\times 10^6$ g./cm.^{2}/%	0.468	0.421	0.448
Breaking stress	$\times 10^6$ g./cm.^{2}	3.33	3.14	3.38
Crimp energy/area	$\times 10^3$ g./cm.^{2}	0.98	1.13	1.07

Processing Behavior

Preliminary Spinning Trial

It was decided to spin the cottons all at one twist rather than at their optimum twists to avoid the effects of differing yarn twists on fabric properties. Accordingly, samples of the three original cottons were submitted to the Clemson Cotton Testing Laboratory of the Agricultural Marketing Service of the U.S. Department of Agriculture for a preliminary spinning trial. The purpose of the trial was to determine the best common twist multiplier to use in spinning the cottons. In this test the cottons were spun into 36/1 yarns at six different twist multipliers. The yarns were tested both for skein strength and for single-end strength and elongation. The Coarse required more twist to reach maximum strength than did Medium and Fine, both of which reached maximum strength at the same twist. Based on the skein strength curves, as shown in the upper part of Figure 2, it was decided to spin at a twist multiplier of 4.50 in the main trial.

The results of the single-end test indicated strength maxima at higher levels of twist than for the skein strength. This effect has been noted by other workers [10].

Full-Scale Processing Trial

1. *Processing Outline.* The cottons were processed in lots of 400 lb. each. Three of the four cottons were tinted prior to picking for identification throughout the trial. Since no more than a gallon of dye solution was added to each lot, the amount of water involved was negligible. The cottons were processed in series through a single-beater picker, carding, two drawings, and roved into 1.70 hank roving. To compensate for the fineness differences, the rovings

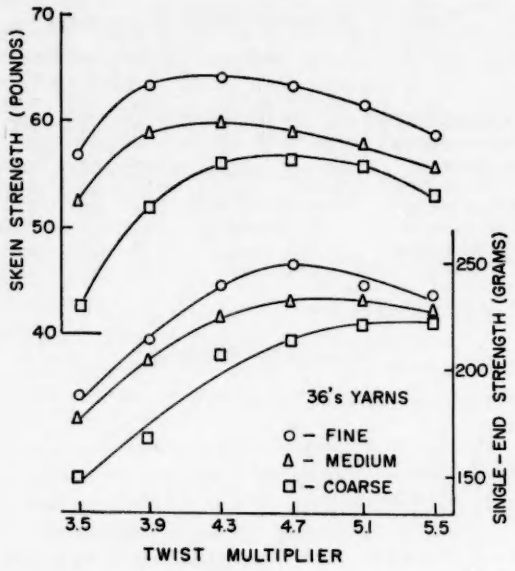

Fig. 2. Effect of twist on skein and single-end yarn strengths from preliminary small-scale spinning trial. Each point on the skein strength curves is the average of at least 25 breaks, and each point on the single-end curves is the average of 30 breaks.

were given different twists (turns per inch) as recommended by Corley *et al.* [9] as follows:

Fine 1.5; Medium 1.6; Coarse 1.7; Blend 1.6

Because there was some doubt as to the spinning characteristics of the Coarse cotton on the available equipment, a preliminary spinning limit trial was performed with an extra bale of the Coarse cotton. From this it was decided that the Coarse could be practicably spun into a maximum count of 30's. Therefore in the main trial, using one spinning frame of 168 spindles, all the cottons were spun into 30/1 yarns at a twist multiplier of 4.50. Spinning ends-down rates were determined while spinning Medium and Blend together, and while spinning Coarse and Fine separately.

Samples of bale cotton, picker lap, card sliver, roving, and yarn were taken for each cotton type for determination of single-fiber properties, group-fiber properties, nep counts, and assembly properties.

The yarns for each cotton type were separated for preparation into warp and filling, and then woven into a 66 × 68 print cloth construction. Lots of 400 yd. of each of the test fabrics were subsequently desized and peroxide bleached together. Half of each

TABLE III. Processing Characteristics

	Coarse	Medium	Fine	Blend	No. tests per sample
Opening waste, %*	3.36	3.46	3.61	—	—
Nep count, neps/grain					
Bale	3.5	6.5	8.8	7.2	12
Card sliver	5.4	10.6	15.3	11.1	12
Roving mechanical properties					
Maximum load, g./grex	0.0183	0.0160	0.0160	0.0182	64
Initial slope, g./%/grex	0.0156	0.0160	0.0181	0.0178	64
Spinning efficiency					
Ends-down/1000 spindle hours	52.3	42.2	18.5	37.9	—
Yarn properties					
Count	30.0	30.1	29.5	30.4	10
Twist, t.p.i.	24.9	24.5	24.8	24.9	25
twist multiplier	4.54	4.47	4.57	4.51	—
Unevenness, Fielden LUE	10.47	10.34	10.12	10.34	100
Single-end strength, g.	180	192	221	193	150
Single-end elongation, %	4.8	5.0	5.5	4.6	150
Weaving warp breaks per 400 yd.†	196	71	36	98	—

* A gross opening loss value, adjusted for differences in moisture content before and after opening. The value for Coarse is an inflated one due to extra waste sustained from a mechanical breakdown.

† The ends used to piece up in tying a broken warp end were treated with an optical bleach which caused the ends to fluoresce under ultraviolet light. Prior to wet finishing, 400 yd. of each of the test cottons were examined under ultraviolet light, with the totals as shown.

of the fabrics was mercerized and then rejoined with the unmercerized goods for dyeing and resin finishing.

The vat dyeing was performed by the pigment-pad, reduced-jig method. The resin used was of the dimethylol ethylene urea type, with a final deposition of about 3%. The goods were cured in tight-strand form at an air temperature of 320° F. for 70 sec. Samples of the fabrics were taken after bleaching, mercerizing, and dyeing, so that of the original 400 yd. of each cotton type, only 60 yd. were resin-treated.

2. *Processing Wastes and Neps.* Due to the limited amounts processed in the trial, a waste check was made only during the opening operation. Opening wastes were found to increase with decreasing Micronaire, as shown in Table III.

Nep counts were made on suitably prepared [13] samples of cotton in bale and card sliver form. Neps increased with decreasing Micronaire, the Fine producing about three times as many neps as the Coarse. However, at a Micronaire of 3.6, the nep level of Fine is not considered to be extremely high [12].

3. *Roving Properties.* There were no differences among the cottons in roving size or unevenness. The roving mechanical properties appear in Table III. These were tested in a standard atmosphere on the Instron Tensile Tester using Cell B, with a gauge length of 10 in., and a cross-head speed of 1 in./min. The relationship between fiber fineness and roving mechanical properties is in this case complicated by the fact that the rovings contained different twists. Thus the small added twist in the Coarse made it substantially stronger, but not stiffer, than the Fine. The Medium and Blend lots were twisted to the same extent. The mechanical properties of the Blend roving were 12% to 14% greater than those of the Medium roving.

A tensile test was also performed in which the twists were altered so that all the cottons were twisted the same. In this test the Fine was better than the Coarse in both strength and slope, by 42% and 66%, respectively.

4. *Spinning Efficiency.* An ends-down check was made with frequency checkers while spinning Medium and Blend on alternate spindles of one frame for a total of 24,696 spindle hours. Although Medium produced 11% more ends-down than the Blend, this difference was not statistically significant. The Fine and Coarse were then spun separately on the same frame for more than 12,000 spindle hours each, with the ends-down record maintained by the operator. The Coarse gave 183% more ends-down than did the Fine, despite the fact that the Fine possessed a poorer fiber length distribution which, according to previous studies [16], should have caused the Fine to spin less well than the Coarse if fineness effects were not involved.

5. *Yarn Properties.* As shown in Table III, the yarns of the test cottons did not differ significantly in size, twist, or unevenness. In single-end strength, however, the Fine yarn was significantly stronger than the yarns of all the other cottons. This test was performed in a standard atmosphere on the Instron Tensile Tester using Cell B, a gauge length of 10 in., and a cross-head speed of 5 in./min. At lower probability levels the difference between Coarse and both Medium and Blend was significant. As Micronaire values decreased, yarn elongation to break was found to increase somewhat. In this case, the elongation of the Blend was less than that of the Medium yarn.

A small test for weaving efficiency was conducted by checking the number of warp yarn breaks for a limited yardage of the test cottons. The Fine showed only 18% as many breaks as did the Coarse, while Medium produced 72% as many breaks as did the Blend.

Fabric Properties

The fabrics were all compared in the dyed state in the following four conditions: Control—mercerized and not mercerized; Resin-finished—mercerized and not mercerized. All tests were carried out in a standard atmosphere.

Tensile and Tear Strength

As in the case of the yarns, the fabrics of the Fine cotton were significantly stronger than those of the other cottons. The strength difference between the Fine and the Coarse was diminished by the weaving and finishing operations, dropping from a 23% superiority for the Fine in the yarn to about 10% in the finished fabrics. The Blend was slightly, but not significantly, stronger than the Medium. The results of two of the strength tests appear in Figure 3, which represents data averaged over warp and filling. Generally the fabrics were stronger in the warp than in the filling direction. Mercerization had no effect on the strength of the control fabrics, but it did significantly reduce the strength loss due to resin finishing. Another test, for ravelled-strip strength, gave similar results.

The results of a single-tongue tear test in the fill-

ing direction appear in Figure 4. In most fabric conditions, Fine was significantly more tear-resistant than the other cottons. There was no difference in the cottons when tested in the warp direction. The fabrics were also subjected to a trapezoid tear test and single- and double-tongue impact tear tests, with results similar to those illustrated. In the interest of brevity, these data have been omitted.

Flex Abrasion Resistance

Prior to resin treatment, the Fine was superior to all the other cottons in resistance to flex abrasion.

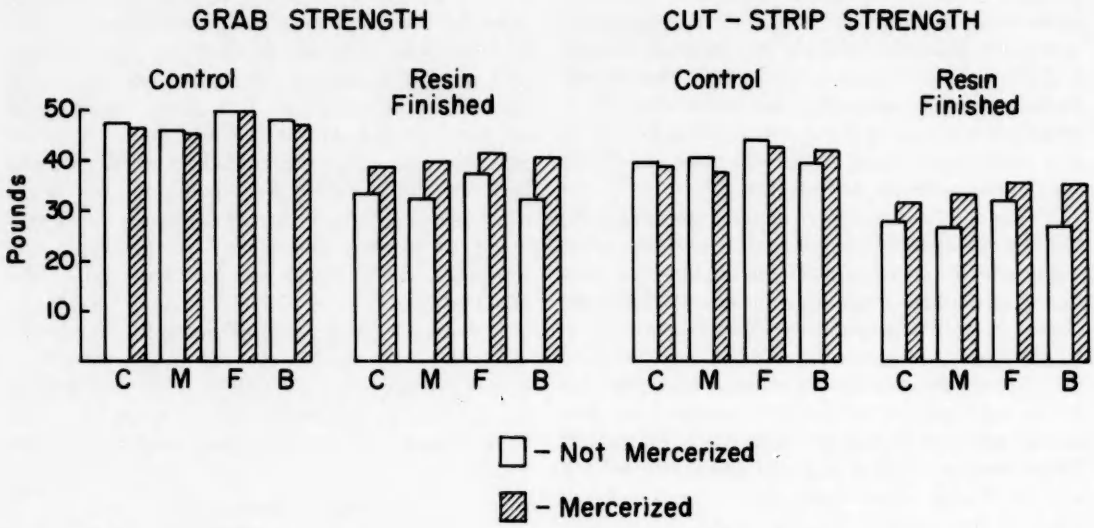

Fig. 3. Comparison of fabric strengths. C—Coarse, M—Medium, F—Fine, B—Blend. The values shown are averaged over warp and filling and are means of 10 grab test and 12 strip test breaks.

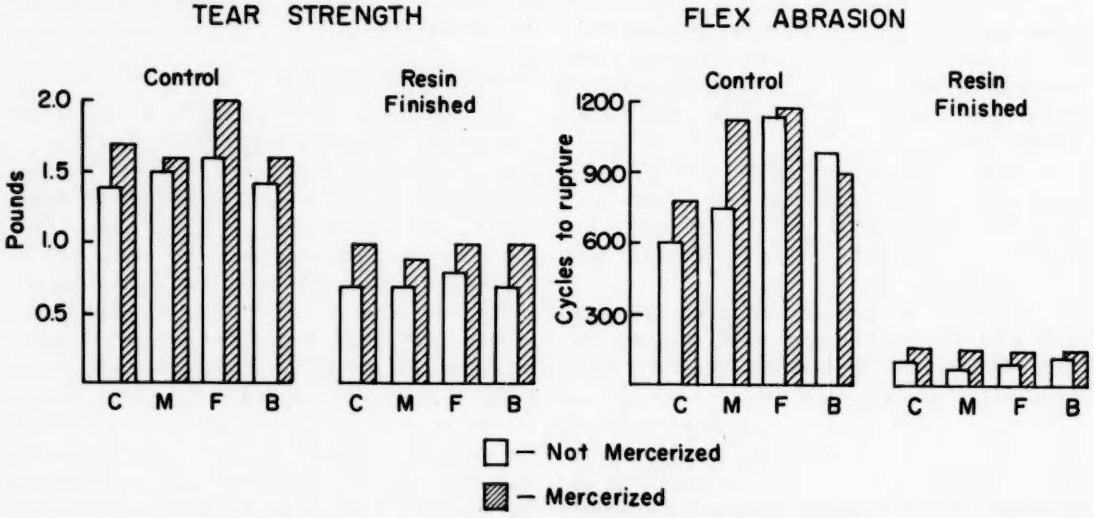

Fig. 4. Effect of fineness on single-tongue tear strength and on flex abrasion resistance. C—Coarse, M—Medium, F—Fine, B—Blend. Both tests were made in the filling direction only. The values are means of 8 tear and 5 flex observations.

However, resin finishing leveled out the differences among the cottons, as illustrated in Figure 4. This test was performed on the Stoll Quartermaster Universal Wear Tester [4] at a fabric tension of 2.25 lb. and a plate pressure of 0.25 lb. It is interesting to note that the abrasion resistance of the Coarse fabric was less reduced with resin treatment than was that of any of the other fabrics. Mercerization improved the abrasion resistance of both the control and the resin-finished fabrics. This improvement with mercerization was much greater for Medium than for the other cottons. A supplementary test produced results in general agreement with the above.

Crease Recovery

The fabrics were tested not only for conventional crease recovery by the TBL method [6], but also for Instron elasticity [8], as shown in Figure 5. The latter test measures the recoverable elasticity after extension to about 50% of breaking elongation. This property has been related to garment appearance, high elasticity being associated with good appearance after wear.

In comparing the cottons, the two test methods produced dissimilar results. By the TBL test, the Coarse was significantly better than the Fine in all fabric conditions. In elasticity, the Fine was definitely superior to the Coarse in the control state but was less elastic after resin treatment. This indicated that the two tests measure somewhat different properties. A similarity between the results of the two methods does exist in that mercerization improved both the elasticity and the recoverability in the control condition, and in that both tests showed this advantage to have been eliminated by resin treatment. Additional tests by the Monsanto method [5] showed no significant differences among the cottons but, otherwise agreed with the TBL test results.

Hand

The evaluation of the "hand" of textiles is largely a subjective matter. The fabrics were placed in pairs before a large number of untrained consumers for rating according to softness. From the results shown in Table IV, the conclusion was drawn that it was possible to distinguish fairly consistently between the cottons in all four conditions. Within a 95% confidence level, the cottons were distinguishable in the following order of decreasing softness: Fine, Medium, Blend, Coarse. It is important to note that the Medium was ranked significantly softer than the Blend.

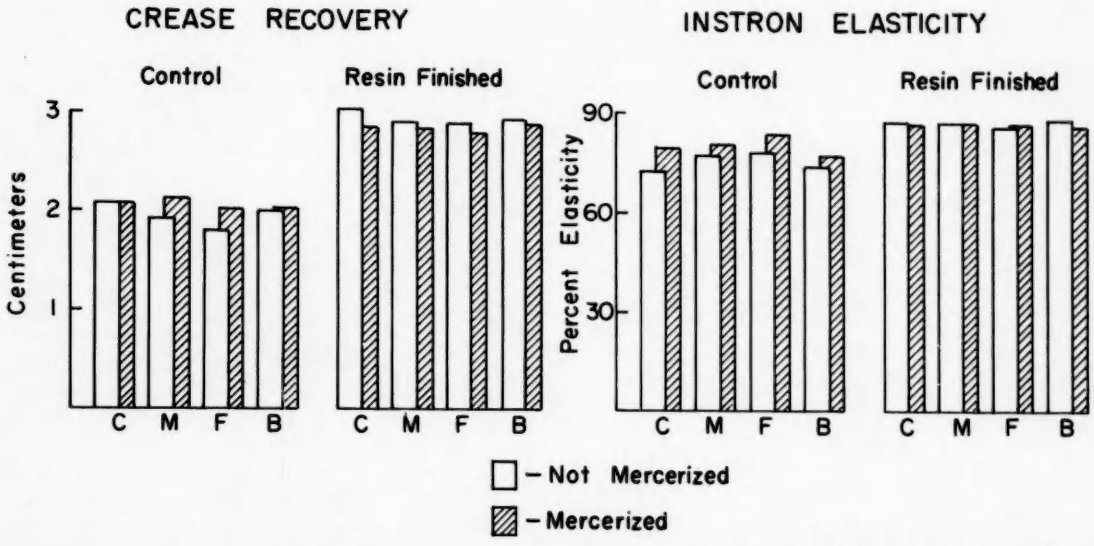

Fig. 5. Effect of fineness on TBL crease recovery and on Instron elasticity. C—Coarse, M—Medium, F—Fine, B—Blend. The values shown are averaged over warp and filling and are means of 8 TBL and 12 elasticity observations.

TABLE IV. Psychometric Evaluation of Relative Softness*

	Number of Judgments "Softer"					
	C vs. M	C vs. F	C vs. B	M vs. F	M vs. B	F vs. B
Control						
Not mercerized	2 vs. 22	0 vs. 24	6 vs. 18	5 vs. 16	17 vs. 3	15 vs. 5
Mercerized	5 vs. 35	2 vs. 30	8 vs. 22	3 vs. 17	19 vs. 7	22 vs. 3
Resin-finished						
Not mercerized	4 vs. 16	0 vs. 20	2 vs. 18	5 vs. 15	20 vs. 5	16 vs. 5
Mercerized	1 vs. 29	3 vs. 17	4 vs. 16	3 vs. 18	19 vs. 6	21 vs. 4

* U.S. Testing Co. data. Observers were asked to judge fabric softness within the pairs of fabric samples. Sample identification: C—Coarse, M—Medium, F—Fine, B—Blend.

In an attempt to confirm the subjective evaluation of observers, the fabrics were tested on the Thwing-Albert Handle-O-Meter [2]. Analysis of the results shown in the upper half of Table V indicated that the Coarse fabric was significantly stiffer than the remaining cottons. All the fabrics were stiffer in the warp than in the filling direction.

In addition to the above tests, two trained observers subjectively rated the fabrics for their "roughness," "stiffness," "thickness," and "resiliency." For the sake of brevity, the data are not given. In general, both observers ranked the Fine as being less rough, less stiff, and somewhat less thick than the other cottons in the control condition. This difference was eliminated by the subsequent wet processing treatments. The resiliency of the fabrics was the same at all processing stations.

It might also be noted that an evaluation of the draping characteristics was performed with the F. R. L. Drapemeter [7]. No significant differences could be observed among the cottons.

TABLE V. Fabric Handle, Shrinkage, and Air Permeability

	Control		Resin-finished	
	Unmerc.	Merc.	Unmerc.	Merc.
Handle-O-Meter (microamperes)				
Warp				
Coarse	61.1	69.7	62.9	79.3
Medium	53.1	68.1	61.6	75.7
Fine	55.9	64.7	68.0	72.0
Blend	56.7	68.0	60.3	74.6
Fill				
Coarse	38.4	41.7	43.1	49.0
Medium	35.8	36.7	39.3	43.6
Fine	33.9	35.6	42.1	43.6
Blend	35.3	41.2	39.8	43.7
Warp shrinkage, %				
Coarse	2.45	0.83	0.78	0.74
Medium	2.97	1.02	0.83	0.92
Fine	3.33	1.99	1.02	1.16
Blend	2.92	1.48	0.92	1.11
Frazier permeability (cu. ft./sq. ft./min.)				
Coarse	107	185	153	207
Medium	85	144	124	208
Fine	87	168	130	200
Blend	93	163	136	208

Shrinkage

In the lower part of Table V appear the results of a shrinkage test on the fabrics. In the warp direction, the fabrics of the Fine cotton shrunk significantly more than those of the Coarse and Medium. The Blend showed slightly more shrinkage than the Medium. Mercerization and resin finishing both reduced shrinkage, but the reductions were not additive. In the filling direction, prior to resin treatment, stretching rather than shrinking took place. These results were confirmed by a second shrinkage test made in a second laboratory.

Air Permeability

Both the Gurley and the Frazier instruments were used to determine the air permeability characteristics of the fabrics. Since both produced parallel results, only data from the latter are shown at the bottom of Table V. The Coarse fabrics are more permeable to the flow of air than are the other fabrics. This might be expected in view of the fact that there are fewer fibers per yarn cross section for the Coarse; and thus there is the likelihood of fewer fiber ends projecting into the interstices of the fabric to restrict the flow of air.

Summary and Conclusions

In this summary the observed effects are discussed in terms of increasing fineness, that is, decreasing Micronaire or decreasing fiber cross-section area.

The advantages of increasing fiber fineness on processing performance are (1) higher roving and yarn strengths, (2) better spinnability with fewer ends-down, (3) lower twists required for maximum yarn strength.

The disadvantages of increasing fiber fineness on processing performance are (1) more neps, (2) more processing waste. It is felt that the waste values might change greatly with different samples and different processing conditions.

The advantages of increasing fiber fineness on fabric performance are (1) increased strength, (2) better abrasion resistance when not resin-finished, (3) better elasticity before resin finishing, (4) a better, softer hand.

The disadvantages of increasing fiber fineness on fabric performance are (1) greater loss in abrasion resistance with resin treatment, (2) less increase in crease recovery with resin treatment, (3) more shrinkage.

In the comparison of Blend with Medium, both cottons were very much alike. The Blend was somewhat stronger and showed greater benefit from the resin finishing. The Medium was more improved by mercerization and was softer to the touch than the Blend. It would appear that further experimentation of the use of fine cottons in a mix with cottons of average fineness would be fruitful.

Although the range of fineness values studied was not so wide as it might have been, some definite advantages have been noted for fine cottons in processing and in fabric properties, especially for those fabrics which are to be used without resin treatment. It must be emphasized, however, that extrapolation of these results may not be valid. As the Micronaire of a cotton falls below 3.5 or 3.0, many of the possible advantages observed herein may be more than offset by an increase in the adverse effects of fineness, such as, for example, nep formation.

On the basis of this study it appears that the cotton manufacturer may not necessarily have to choose between processing facility and fabric quality. With the exception of neps, both can be improved by the judicious use of finer cottons. Furthermore, it is conceivable that more extensive study of the nepping problem may provide some means whereby the nepping characteristics of fine cottons may be reduced.

Acknowledgment

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A New Cotton Lustermeter

Abstract

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Abstract of paper given at the Cotton Research Clinic, February 15–17, 1956, Pinehurst, N.C.

A SINGLE answer, direct-reading instrument especially adapted for measuring luster of raw cotton and gray and mercerized yarns has been developed. (The instrument was demonstrated at Pinehurst.) It includes a special sample clamp, which fits into a turret top holder on the instrument that may be turned through 180° for measurement of the sample with threads or fibers facing first in one direction, then in the opposite direction (as a check on sample preparation). The sample is illuminated at 45°, and the light leaving the sample is measured at 0° (diffuse) and at 45° (specular). By means of a special circuit the ratio of the two is read directly from an automatically indicating scale. The scale reads in terms of per cent luster, 100% for high luster, 0 for zero luster, according to the formula 100 $(1\text{-}D/S)$, in which D is the diffuse reflectance and S the specular reflectance. Samples are quickly and easily prepared from yarn skeins on special holders, and a similar though narrower holder is used for measuring combed fibers from pinches of blended raw stock samples.

The instrument is an adaptation of a simplified all-purpose gloss meter under development by R. S. Hunter.

Measurements are being made on all raw stock and gray yarn samples of the 1955 Standardized Variety cottons, and on all mercerized yarns in finishing tests made on this series. The following preliminary data show the general use of the instrument and the general level of results obtained.

			Per cent luster			
			Grey yarns			
			22's		50's	Merc. yarn 50's
Variety	No. of samples	Raw cotton	Carded	Combed		
Acala 1517	27	61	31	32	33	43
Delfos	27	58	31	32	33	41
Acala 4–42	21	59	31			
DPL	114	59	31			
Coker	51	58	32			
Pima	12	67			40	51

A full description of the instrument and of basic goniophotometric studies on cotton yarns and fibers, together with luster measurements obtained on the 1955 Standardized Variety, will be reported at a later date.

Effect of Cotton Fiber Bundle Break Elongation and Other Fiber Properties on the Properties of a Coarse and a Medium Singles Yarn[1]

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Southern Regional Research Laboratory,[2] New Orleans, Louisiana

Abstract

Forty-three cottons, varying extensively in fiber properties, were used to show the relationship between cotton fiber properties, particularly fiber bundle break elongation, and the properties of a coarse and medium yarn. In addition, there are presented some practical aspects of a speculative nature based on the results. The cottons were processed into a series of yarns of varying twists. Fiber break elongation, along with five other fiber properties (length, fineness, strength, length variability, and maturity), was correlated with yarn break elongation at twists for maximum skein strength, maximum single strand strength, and at two constant twists (4.00 and 5.00 T.M.).

It was found that yarns produced from these cottons varied considerably in strength and elongation at break. Yarn strength and break elongation were found to be directly related for the commercially grown short and medium staple cottons, but the long staple and the experimental, strong-fibered cottons were found to be anomalous in that they produced yarns whose strength was disproportionate to their fiber break elongation. Based on multiple correlation analyses, fiber break elongation ranked first and strength ranked second in importance as contributors to yarn elongation for a 30/1 yarn at twists for maximum strength.

Secant modulus (average stiffness) and "toughness" index of fibers and yarns are suggested as quality indices for evaluating processing efficiency. This study also demonstrated the necessity of controlling carefully spinning and other processing conditions in evaluating the elastic properties of cotton yarns.

Introduction

Fiber properties are known to be the main determinants of yarn quality with length, fineness, strength, maturity, and grade contributing materially, although in different orders of importance [2, 3, 6 through 8, 19, 20, 22, 23]. These fiber properties, however, on a collective basis and under even ideal conditions, still leave approximately 20% of the variance of spinning quality unaccounted for [5]. Therefore, certain fiber properties other than those which have been studied extensively must contribute to yarn quality and obviously to processing efficiency as well.

Considerable emphasis has been given to correlating cotton fiber property combinations with end-use requirements and quality [23], whereas the need for determining the combinations of fiber properties required to maintain maximum operating efficiency has been recognized only recently. All too frequently the proper combination needed to meet one of these objectives may preclude attainment of the other. Fiber properties should therefore be considered as being dual functional, with contributions being made toward processing efficiency and toward product quality.

The dynamic nature of spinning and subsequent textile operations, whose efficiencies depend to a certain extent on the absorption of energy to maintain specified levels of operating efficiency, should mandatorily lead to a consideration of the elastic properties of fibers and yarns, which are energy absorptive in nature, and to those quality parameters reflecting this yarn property.

[1] Presented by Louis A. Fiori at the Cotton Research Clinic, Pinehurst, North Carolina, February 15–17, 1956.

[2] One of the laboratories of the Southern Utilization Research Branch, Agricultural Research Service, U.S. Department of Agriculture.

Textile manufacturers refer to the amount of "stretch" required in yarns, the per cent take-up or contraction in the weaving and finishing operations, and "sewability" of threads. These imply functional use of yarn elasticity (co-function of strength and elongation), in addition to strength, as evaluating media, even though the latter property is in the majority of cases the only one measured and considered.

Textile scientists have given considerable attention to those properties which logically might affect energy absorption operations of textile fibers and yarns. Many early attempts were made to identify the factors which influence the elastic properties of textile fibers [4, 10, 12, 17, 24]. More recently, efforts in this field have been directed toward correlating the breaking strength and elongation of textile fibers with mechanical processing characteristics and with certain elements of product quality [9, 11, 14 through 16, 22].

The measurement of single cotton fiber break elongation has been tedious and performed successfully in isolated instances on single fibers [8, 13, 15, 22]. Recently, however, the availability of a rapid method for determining fiber bundle break elongation [21] and the increasing realization that yarn elongation in addition to strength should be used to evaluate the processing performance of cottons has produced an increase in efforts to correlate the elastic properties of cotton fibers with the elastic properties of yarns and with processing efficiency.

This study shows the relationship between cotton fiber properties, particularly bundle break elongation, and the properties of coarse and medium yarns, and attempts to present some practical aspects of a speculative nature based on the results. Subsequent reports will cover comparable evaluations and analyses of the remaining yarns processed in this study: 40/1, 60/1, 80/1, and 100/1 yarns.

Samples

Forty-three cottons were evaluated, including experimental as well as normal cottons used in the textile industry. These cottons had wide ranges in each of the important fiber properties, with Table I showing a summary of conventional fiber properties. For these cottons, it is noted that the high and low fiber break elongation values differ by approximately 100%. Since this range is consistent with that available in both normal and experimental cotton varieties, it was possible to establish the effect of fiber elongation at break on selected yarn properties. The ranges in other fiber properties are also considered representative and provide reliable bases for the correlations made in this study.

Experimental Procedure

Processing

About 15 lb. of each cotton was processed on conventional processing equipment into 15/1 and 30/1 yarns. These yarns were spun with a series of twist multipliers in 0.2 T.M. increments, which assured reliable and uniform twist-strength and twist-elongation curves. Spinning conditions (tensions, speeds, etc.) were held constant for all the cottons so that the two quality parameters evaluated, strength and break elongation, would be influenced by the properties of the cottons rather than by mechanical factors. Additionally, the use of small increments of

TABLE I. Summary of Fiber Property Ranges

Fiber property	Range from	Range to
Length		
Classer, in.	29/32	1-3/4
Suter-Webb,		
U. Q., in.	0.88	1.95
Mean, in.	0.72	1.60
C. V., %	22	37
Fibrograph		
U.H.M., in.	0.82	1.58
Mean, in.	0.65	1.20
U.R.	87	74
Fineness		
Suter-Webb, μg./in.	2.4	8.0
Micronaire Index, Upland, curvilinear	2.7	7.1
Arealometer		
Specific area, $mm.^2/mm.^3$	598	356
Maturity		
Sodium hydroxide method, %	96	55
Strength and elongation		
Pressley Index, lb./mg.	6.7	10.7
Stelometer		
Tenacity, g./grex		
0 in.	3.2	4.7
1/8 in.	1.7	3.2
Elongation, %		
0 in.	—	—
1/8 in.	5.9	11.2

twist permitted the selection of reliable averages of maximum skein and single strand strength values and of the corresponding yarn break elongation values. Similar data were selected from the twist-strength curves at points of constant twist (4.00 and 5.00 T.M.). Break elongation data were obtained in conjunction with single strand strength determinations and were used in conjunction with both skein and single strand strength data as a basis of the statistical analyses and of calculating secant modulus (average stiffness) [18].

Testing

Skein strength determinations were made on a pendulum-type tester of 0 to 150-lb. capacity [1*a*], and single strand strength and break elongation measurements were made on an automatic Uster [3] single strand tester. Fiber properties measured with the Stelometer [15, 21] were obtained from samples of card sliver. All other fiber properties were determined by ASTM methods [1*b*] and were obtained from samples of raw stock.

Description of Terms

Twist multiplier, as used in this report, is based on so-called nominal twist and yarn number (indicating amount of twist desired and the yarn number to be spun) in contrast to machine twist and yarn number, actually measured.

Tenacity (breaking) for fibers and yarns is defined in terms of force per unit linear density, as grams per grex, or as count strength product (break factor).

Secant modulus is defined as the ratio of change in stress to change in strain between two points on a stress-strain diagram, particularly the points of zero stress and breaking stress [1*c*]. This is sometimes referred to as average stiffness and defined, generally, as the resistance to deformation of textile products [18]. Stress was calculated as tenacity (count-strength product) and then converted to grams per grex for both skein (per single end basis) and single strand test values in order to have these data in terms similar to the fiber tenacity data. Strain (yarn break elongation) was obtained in conjunction with the single strand strength data, and inasmuch as stress-strain relationships of cotton yarns are approximately linear, use of the elongation values at break as a basis for calculating modulus is considered valid.

Toughness Index, as referred to in this study, represents a measurement of the area under the stress-strain curve from the origin to the breaking point. It defines generally the ability of a material to absorb work. It is obtained by multiplying breaking strain times breaking stress divided by two [18].

Maximum skein and single strand strength values are estimates obtained from the center portion of the so-called "maximum strength plateau."

[3] The use of trade names does not imply their endorsement by the Department of Agriculture over similar products not mentioned.

Analysis of Data

Since fiber break elongation values for the cottons used covered a range of approximately 100%, it was possible to study the effect of this property on yarn break elongation, and to a limited extent, on yarn strength at various twists. Other fiber properties were also related to yarn elongation.

A number of different cotton groups were selected from the series to illustrate that (1) a wide range of yarn break elongations is available for selection, independent of other fiber properties such as staple length; (2) that various combinations of relatively high or low yarn breaking strengths and elongations at break can be obtained. For the normal cottons or for all cottons used in this study there are shown (*a*) general relationships between yarn break elongation and strength; (*b*) specific relationships of fiber break elongation to yarn break elongation; (*c*) relationship between fiber secant modulus and yarn secant modulus, based on simple correlations; and (*d*) relationship of selected fiber properties to yarn break elongation and yarn secant modulus, based on multiple correlations.

Ranges in Yarn Break Elongation

Figure 1 shows ranges of yarn break elongations for a selected group of staple lengths. At a given twist multiplier, it is apparent that significant differences exist in yarn break elongation values between cottons which are independent of the widely different staple lengths. Generally these differences increase with increases in twist, as would be expected, since the twist-elongation relationship is parabolic in nature. Obviously, however, within the range of twist normally used, this relationship may be considered linear for all practical purposes.

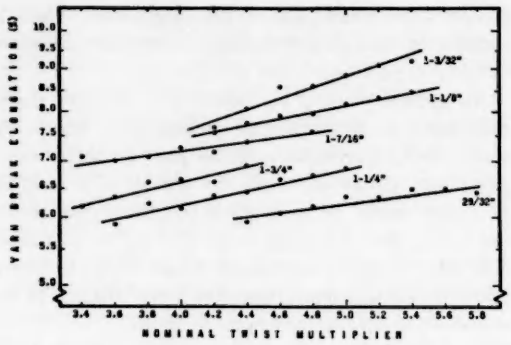

Fig. 1. Yarn break elongations for various staple lengths and twists for a 30/1 yarn.

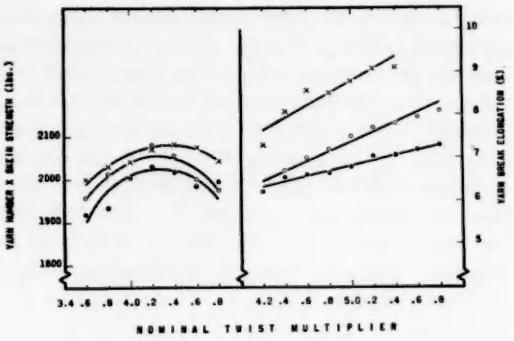

Fig. 3. Cottons producing yarns of approximately the same strength but different elongations for a 30/1 yarn.

Analysis of a similar plot, based on 15/1 yarns from the same cottons, reveals no significant changes in these relationships between staple lengths, twists, and yarn break elongations.

That significant differences may exist (from 30 to 50%) in elongation values regardless of staple lengths and twists indicates the necessity of considering this property as a contributing factor to processing performance and product quality. The apparent lack of correlation between staple length and yarn break elongation may preclude the prediction of yarn break elongation for any staple length.

Yarn Strength-Elongation Combinations Possible

Figure 2 shows a series of yarns differing significantly in strength but being about equal in yarn elongation. It should, therefore, be recognized that there are cottons having fiber property combinations which spin into such types of yarns. While it might be generally expected that the yarn with the highest strength would process the most efficiently, consideration should be given to the modulus or average stiffness values of those cottons. On the basis of the definition of secant modulus, it is possible that the yarn having the lowest strength-elongation ratio may process as efficiently, if not more so, than the other two yarns.

Another series of yarns, differing little in strength but differing appreciably in yarn elongation, is shown in Figure 3. Perhaps the yarn with the highest elongation and lowest modulus would be expected to spin more efficiently since it might tend to deform more readily during the spinning and subsequent operation. In Figure 4 are shown two yarns, one having relatively high strength–low elongation properties and the other having relatively low strength–high elongation properties. These two cottons represent extremes in the characteristic of mod-

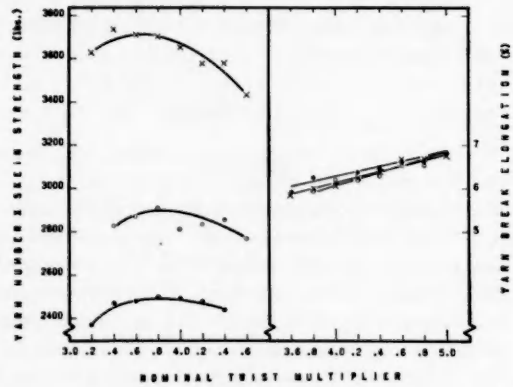

Fig. 2. Cottons producing yarns of different strengths but the same elongation for a 30/1 yarn.

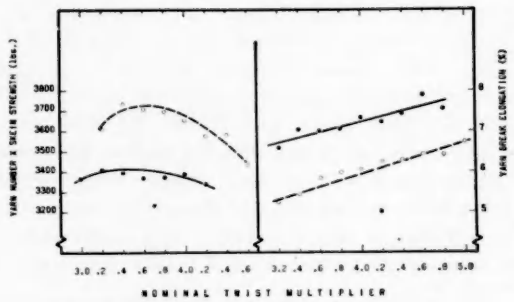

Fig. 4. Cottons producing 30/1 yarns of inverse strength-elongation relationships.

ulus or average stiffness. As a result, it might be hypothesized that the yarn of low modulus properties would process more efficiently or just as efficiently as the yarn of high modulus properties, notwithstanding the higher strength of the latter yarn. Incidentally, the low modulus yarn also has a relatively high toughness index value which indicates an ability to "take it" and probably to process more efficiently than the high modulus yarn in spite of the high strength of the latter yarn. Figures 2 through 4 show that from available cottons in use today at least three different types of yarn may be manufactured, with the processing efficiency of each depending on its own peculiar yarn strength-elongation properties. The conclusion made for the 30/1 yarn (Figures 2 through 4) is substantiated by analysis of data for the 15/1 yarn, which is not shown in this report.

General Relationships between Yarn Break Elongation and Strength

The correlation between yarn elongation and strength within a section of yarn is considered good since twist and fiber properties are held constant. However, since fiber properties are known to influence the characteristics of the stress-strain curve, the relationship between yarn elongation and strength for different sections of yarns manufactured from a series of cottons will be dependent necessarily on the contribution made by the respective fiber properties of the cottons used. In Figures 5 through 8 which follow, the regression lines were computed by the method of least squares. Confidence limits are based on twice the standard error of the estimate of the dependent variable.

Figure 5 shows relationships existing between yarn break elongation and maximum skein strength for a series of cottons differing in fiber properties. The cottons are classified into three distinct groups —normal, long staple, and experimental. By normal cottons are meant well-known varieties ranging in staple length between $\frac{29}{32}$ to $1\frac{1}{8}$ in., normally in abundance commercially; by long staple is meant the Pima and Karnak type cottons; by experimental are meant those varieties not yet commercially available, possessing relatively high strength.

A comparatively good, positive correlation exists between yarn elongation and strength for yarns spun from the normal cottons as represented by a simple correlation coefficient of 0.797. This coefficient, as well as those that follow, is considered to be statistically significant at either the 95 or 99% probability level. It should be observed that a small change in yarn break elongation, based on varietal differences, is associated with a significant change in yarn strength. As a result, yarn break elongation deserves more attention as an index of yarn quality.

Yarns spun from the long staple cottons exhibited an inverse relationship of yarn elongation to yarn strength when all of these yarns were disassociated from yarns spun from the normal cottons. Since only a few long staple cottons were used, however, the inverse relationship shown for this evaluation should be accepted with reservations.

Yarns spun from the experimental cottons, also, were distinctly separated from yarns spun from the normal cottons in a somewhat inverse relationship of yarn elongation to yarn strength. As with the long staple cottons, the limited number of experimental cottons used places some reservation on the inverse relationship shown.

Two cottons (identified by + marks on the chart) spun yarns of relatively high elongation but low strength properties, almost causing yarns to form a fourth group of values. One of these varieties was a very coarse Peruvian type which would tend to explain its low yarn strength. The other was a variety normally raingrown which was grown under irrigated conditions.

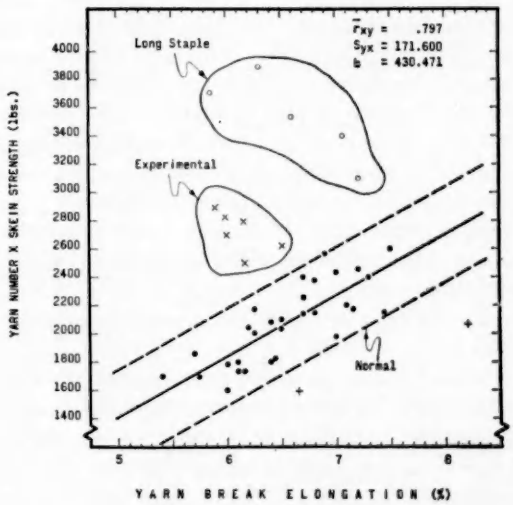

Fig. 5. Yarn skein strength–break elongation relationships based on twists for maximum strength for a 30/1 yarn.

These data and similar data for the 15/1 yarn clearly indicate that there is a definite limit to yarn break elongation values that can be obtained from fiber property combinations found in available cottons. This limit is approximately between 5.5 and 7.5% for the 30/1 yarn and between 6.5 and 8.5% for the 15/1 yarns. Interestingly enough, even experimental cottons having extremely high fiber strength and cottons which are extremely long and fine failed to produce yarns outside the limits shown.

The grouping effect is explained by the contribution made to yarn strength by such fiber properties as strength, length, and fineness, which placed the yarns in a completely separate bracket solely because of the contribution of these fiber properties to yarn strength. If it can be shown that additional break elongation in yarns is required for increased processing efficiency or to satisfy some quality requirement, breeders will have to explore the possibility of increasing the elongation-strength ratio of the cotton fiber; or such factors as drafts, roving twists, spinning tensions, etc. will have to be studied as contributing to this yarn property.

The relationships between yarn elongation and maximum single strand strength are similar and therefore no plots are shown. It is technologically significant that two independent test methods (skein and single strand) for yarn strength show identical results in classifying the cottons by groups. The simple correlation coefficients for the normal cottons are about equal to 0.797 for skein and 0.810 for single strand), indicating excellent agreement in ranking the two methods of test. An interesting difference not affecting the over-all results is that yarn elongation values of corresponding cottons for the single strand method of test are higher than those for skein. This, of course, is due to the higher twist required to obtain maximum single strand strength as compared with that required to obtain maximum skein strength, and to the fact that elongation increased linearly with twist.

Similar groupings of the cottons resulted when data for the 15/1 yarn were plotted. Here, again, the simple correlation coefficients for the normal cottons showed good agreement between the two methods of test, being 0.546 for skein and 0.450 for single strand.

Specific Relationships between Fiber and Yarn Break Elongation

Figure 6 shows the relationship of fiber break elongation to yarn break elongation at twists for maximum skein and single strand strength. The simple correlation coefficients are 0.675 for skein strength and 0.715 for single strand strength. The normal cottons are scattered throughout the range of fiber elongation values, indicating a varietal or environmental effect rather than a fiber property effect. This hypothesis is further substantiated on examining the values of the long cottons which also show a wide scatter of values. The experimental cottons, however, tend to group and be relatively low in fiber elongation. These are relatively high strength cottons so there may be a logical explanation for the "grouping" effect and low elongation values, since such cottons normally do not possess high elastic properties.

In examining similar plots of data based on 15/1 yarn, lower correlations between fiber and yarn break elongations were apparent. However, the two methods of test again showed good agreement, with the correlation coefficients being 0.619 for skein and 0.549 for single strand.

A large change in fiber break elongation is associated with a small change in yarn break elongation,

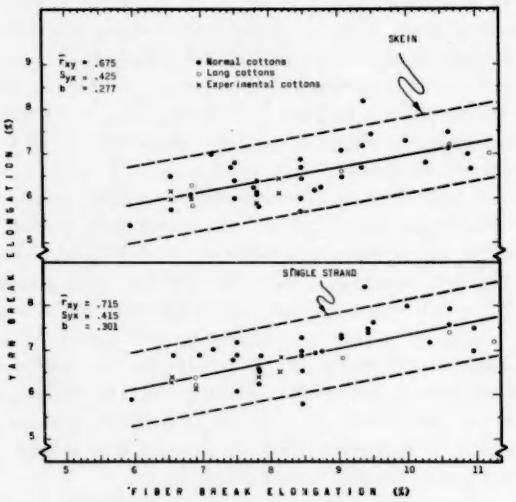

Fig. 6. Effect of fiber break elongation on yarn break elongation at twists for maximum skein and single strand strength for a 30/1 yarn.

which might indicate the need for drastic differences, from a breeding standpoint, in fiber break elongation if significant differences in yarn break elongation are to be realized. However, since it was shown in Figure 5 that small differences in yarn break elongation are associated with relatively large changes in yarn strength, the importance of fiber elongation as a secondary contributor to yarn strength becomes obvious. As a matter of fact, a plot of yarn strength as a function of fiber elongation (not shown) shows a simple correlation coefficient of 0.655 for the normal cottons and appreciable changes in yarn strength due to changes in fiber elongation.

When yarn break elongation is shown as a function of yarn strength (Figure 5), the cottons are classified or grouped according to genetic characteristics; whereas when yarn break elongation is shown as a function of fiber break elongation, no such grouping occurs. An observation which may have practical significance is that the normal cottons have fiber break elongation characteristics which cover practically the whole range included in this study (6.0 to 10.9%). This may indicate some environmental as well as varietal influences insofar as fiber break elongation properties are concerned. This range in fiber break elongation of the normal cottons may offer a lead to the solution of blending incompatibilities exhibited by certain particular cotton varieties, since the blending of fibers which differ appreciably in load-extension characteristics is not recommended [13].

The experimental cottons, which in this case represent essentially "high strength" varieties, are apparently relatively low in fiber break elongation characteristics. On the other hand, the long staple cottons, like the normal cottons, covered the range of fiber break elongations studied.

The relation of fiber to yarn break elongation at constant twists was also investigated. Figure 7 shows that at a constant twist (4.00 T.M.) the simple correlation coefficient relating fiber to yarn break elongation is 0.694. These two properties were also correlated at another constant level of twist (5.00 T.M.) with similar results (simple correlation coefficient of 0.659). The simple correlation coefficients for the 15/1 yarn were 0.646 for the 4.00 T.M. and 0.538 for the 5.00 T.M. The good correlation between fiber and yarn elongation at a number of selected levels of twists is probably due to the relationship between twist and yarn elongation which is described by a family of linear and almost parallel lines for a series of cottons (Figure 1).

Relationship between Fiber and Yarn Secant Modulus

Secant modulus defines the elastic properties in terms of "average stiffness" and resistance to deformation of fibers and yarns; the relationship of fiber to yarn secant modulus was investigated using as a basis twists for maximum skein and single strand strength.

Figure 8 shows a plot of fiber versus yarn average stiffness at twists for maximum single strand

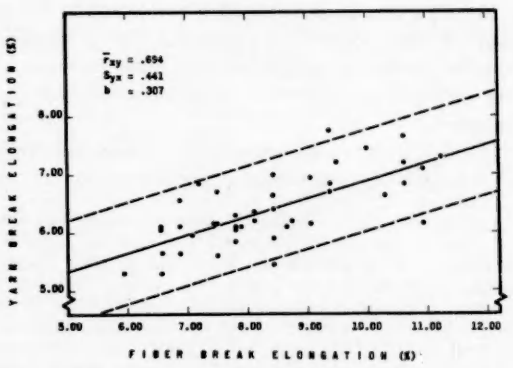

Fig. 7. Effect of fiber break elongation on yarn break elongation at constant (4.00 T.M.) twist for a 30/1 yarn.

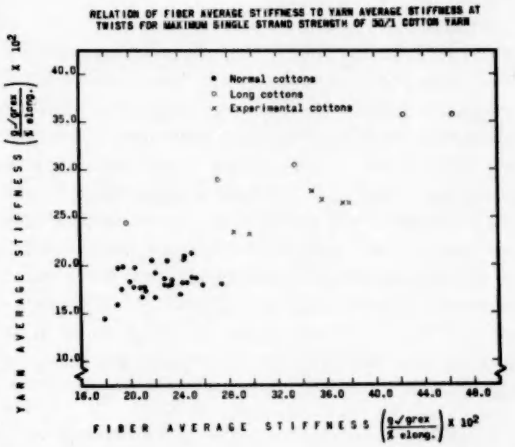

Fig. 8. Relation of fiber average stiffness to yarn average stiffness at twists for maximum single strand strength for a 30/1 yarn.

TABLE II. Multiple Correlation of Yarn Break Elongation with Selected Fiber Properties for a 30/1 Yarn [1]

Variables correlated		Skein		Single strand	
Dependent	Independent	Coefficient of multiple correlation	Beta coefficients	Coefficient of multiple correlation	Beta coefficients
Yarn	*Fiber*				
Break elongation	Elongation	0.713	0.647	0.743	0.673
	Tenacity (1/8-in. gauge length)		−0.415		−0.449
	Weight fineness		−0.260		0.283
	Length (upper quartile)		0.259		−0.180
	Length variability		−0.155		−0.136
	Maturity (NaOH)		−0.091		−0.082
Break elongation	Elongation	0.709	0.558	0.738	0.575
	Tenacity (0-in. gauge length)		−0.344		−0.374
	Weight fineness		−0.295		0.129
	Length (upper quartile)		0.117		−0.220
	Length variability		−0.131		−0.109
	Maturity (NaOH)		−0.073		−0.060
Break elongation	Elongation	0.720	0.644	0.743	0.671
	Tenacity (1/8-in. gauge length)		−0.467		−0.489
	Fineness (Micronaire)		−0.311		0.366
	Length (Fibrograph mean)		0.345		−0.186
	Length variability		−0.155		−0.115
	Maturity (NaOH)		−0.033		−0.073

[1] Based on 43 cottons and on twists for maximum skein and single strand strength.

strength. It is evident that a relationship exists between these two properties, as indicated by the simple correlation coefficient of 0.854. A comparable plot on the relationship of twists for maximum skein strength is not shown since it so nearly repeated that shown in Figure 8.

Unless interpreted correctly, Figure 8 may be somewhat misleading. The normal, experimental, and long staple cottons group into three different modulus categories. The important relationship to observe is that those cottons that have a low fiber average stiffness tend to have a low yarn average stiffness, while those that have a higher fiber average stiffness also tend to have a higher yarn average stiffness. The experimental cottons react similarly to the normal cottons in having stiffness ratios within a narrow range but at a higher level. This is important from a breeding standpoint because it indicates that breeders should consider not only fiber strength, but strength as related to elongation.[4]

[4] The normal cottons are naturally concentrated in the lower end of Figure 8 because the relationship between fiber elongation and strength and yarn elongation and strength varies only within a narrow range for these cottons. It is, therefore, evident from the chart that correlation between fiber and yarn average stiffness for normal cottons alone would be very poor. Actual computations using only the data for normal cottons resulted in a correlation coefficient of 0.254. On the other hand, when data on fiber average stiffness and yarn average stiffness for normal cottons were averaged and used as only one cotton, along with the eleven long staple and experimental cottons, a correlation coefficient of 0.815 resulted. Although this is slightly lower than the coefficient of 0.854 obtained when all 43 cottons were included and is based on a smaller number of observations, the results are significant and confirm the conclusions mentioned in the text.

Relationship of Selected Fiber Properties to Yarn Break Elongation and Yarn Average Stiffness by Use of Multiple Correlation Techniques

Thus far, simple correlation techniques have been employed to relate the fiber and yarn properties studied with promising results being obtained. It is realized, however, that fiber properties other than elongation and strength may have contributed to the properties of the yarns studied. Therefore, multiple correlation was used to estimate the extent to which a given yarn property is associated with a specified number of fiber properties and to rank the effect of the various fiber properties in the order of their importance.

Table II shows the results of separate multiple correlations of yarn break elongation with six se-

lected fiber properties for a 30/1 yarn based on twists for maximum skein and single strand strengths.

In those correlations, the following six fiber properties were used as independent variables: elongation, tenacity, fineness, length, length variability, and maturity. The first two correlations for both skein and single strand utilized what are considered to be the more precise techniques for measuring the fiber properties of length and fineness. The only difference between these two correlations is that in the first case tenacity was measured at $\frac{1}{8}$-in. gauge; in the second, 0-in. gauge length. In Tables II and III such changes in an independent variable are indicated by italicizing the changed variable. A change from $\frac{1}{8}$- to 0-in. gauge length had very little effect on the multiple correlation coefficient as evidenced by the small change in value. The multiple correlation coefficients, 0.743 and 0.738 for single strand and 0.713 and 0.709 for skein, respectively, were statistically significant. In all cases the Beta coefficients indicated that fiber elongation is the most important contributing property to yarn break elongation, with tenacity being next. Weight fineness and length compete in most cases for third and fourth place in importance. The Beta coefficients also show an inverse relationship between yarn break elongation and fiber tenacity and this yarn property and weight fineness.

The third correlation utilizes the same fiber properties as the first except that fiber fineness is measured by the Micronaire and length by the Fibrograph methods of test. Here, again, the multiple correlation coefficients are about the same as those obtained for the other two correlations. Also, Beta coefficients indicate, again, that elongation and tenacity are the two most important fiber properties contributing to yarn elongation, which is significant since the more practical test methods for fiber fineness and length were used.

Table III shows the results for a 15/1 yarn based on a similar analysis (on twists for maximum skein and single strand strength) to that made for the 30/1 yarn (Table II). Fiber elongation and tenacity still rank first and second in importance in their effect on yarn elongation. The only other difference of any consequence is that fiber fineness is of somewhat lesser importance as a contributing factor to 15/1 yarn elongation than to 30/1 yarn elongation. As in the case of the analyses made for the 30/1, the substitution of the more practical test methods for measuring fineness and length did not alter the rank of the two most important properties.

TABLE III. Multiple Correlation of Yarn Break Elongation with Selected Fiber Properties for a 15/1 Yarn [1]

Variables correlated		Skein		Single strand	
Dependent	Independent	Coefficient of multiple correlation	Beta coefficients	Coefficient of multiple correlation	Beta coefficients
Yarn	*Fiber*				
Break elongation	Elongation	0.667	0.650	0.617	0.566
	Tenacity (1/8-in. gauge length)		−0.360		−0.416
	Length (upper quartile)		0.282		0.357
	Maturity (NaOH)		−0.186		−0.205
	Weight fineness		−0.101		−0.087
	Length variability		−0.018		−0.033
Break elongation	Elongation	0.667	0.558	0.627	0.429
	Tenacity (0-in. gauge length)		−0.319		−0.426
	Length (upper quartile)		0.182		0.238
	Maturity (NaOH)		−0.169		−0.148
	Weight fineness		−0.117		−0.161
	Length variability		0.003		−0.028
Break elongation	Elongation	0.666	0.655	0.605	0.594
	Tenacity (1/8-in. gauge length)		−0.388		−0.393
	Length (Fibrograph mean)		0.323		0.312
	Maturity (NaOH)		−0.182		−0.188
	Fineness (Micronaire)		−0.124		−0.151
	Length variability		0.001		−0.015

[1] Based on 43 cottons and on twists for maximum skein and single strand strength.

An interesting comparison of multiple correlation coefficients of the 30/1 and 15/1 yarns, irrespective of the bases (test method) used for analyses, is that the over-all correlation is somewhat better for the finer yarn (Tables II and III).

Since the variables correlated thus far left between 50 and 60% of the variance of yarn elongation unexplained, an effort was made to include still other sources of variation in the analyses. This was accomplished by considering yarn strength and elongation jointly in appropriate units in terms of yarn average stiffness. Similarly, fiber tenacity and elongation were considered jointly as one variable in terms of fiber average stiffness along with fineness, length, maturity, and length variability. Table IV shows the results of replacing yarn elongation with yarn average stiffness as the dependent, and fiber elongation and tenacity with fiber average stiffness as one of the independent variables in a multiple correlation analysis for a 15/1 and a 30/1 yarn for the skein and single strand methods of test. A substantial increase in the multiple correlation coefficient to approximately 0.95, for both yarn numbers, and a resultant coefficient of determination (multiple correlation coefficient squared) of about 0.90 leaves only approximately 10% of the variance in the dependent variable unexplained. Fiber average stiffness naturally ranks as the most important variable by either method of test. An exception was a slightly lower multiple correlation coefficient (0.927) for the single strand method of test for the 15/1 yarn, but this correlation still leaves only 14% of the variance in the dependent variable unaccounted for.

Because of the promising results obtained when fiber and yarn average stiffness values are used for this type of analysis, further consideration should be given to use of this approach as a step in accounting for a larger percentage at the variation in yarn break elongation and strength.

Discussion of Results

These results indicate that available cottons, normal and experimental, do differ enough in fiber bundle break elongations and resultant yarn break elongations to consider these fiber and yarn properties as important contributing factors to processing efficiency, and possibly, to product quality.

The maintenance of efficiency in operation of the spinning and subsequent textile processes depends to a certain extent on the ability of the textile material to absorb dynamic stresses. This fact should war-

TABLE IV. Multiple Correlation of Yarn Average Stiffness with Selected Fiber Properties [1]

Variables correlated		30/1 yarn		15/1 yarn	
Dependent	Independent	Coefficient of multiple correlation	Beta coefficients	Coefficient of multiple correlation	Beta coefficients
		Maximum skein strength			
Yarn	*Fiber*				
Average stiffness[2]	Average stiffness[4]	0.958	0.552	0.949	0.641
	Weight fineness		−0.320		−0.300
	Length (upper quartile)		0.252		0.155
	Maturity (NaOH)		0.215		0.203
	Length variability		−0.134		−0.165
		Maximum single strand strength			
Yarn	*Fiber*				
Average stiffness[3]	Average stiffness[4]	0.961	0.598	0.927	0.669
	Weight fineness		−0.339		−0.301
	Length (upper quartile)		0.199		0.067
	Maturity (NaOH)		0.184		0.263
	Length variability		−0.156		−0.137

[1] Based on 43 cottons.

[2] Based on maximum skein strength and on elongation at break at twists for maximum skein strength.

[3] Based on maximum single strand strength and on elongation at break at twists for maximum single strand strength.

[4] Based on Stelometer ratios of tenacity and break elongation at 1/8-in. gauge length. Average stiffness is the ratio of change in stress to change in strain between two points on a stress-strain diagram, particularly the points of zero stress and breaking stress.

rant consideration being given to the elastic property of yarn, in addition to its tensile strength, as contributing to processing efficiency. Such quality indices as average stiffness, defining the resistance to deformation of fibers and yarns, and toughness index, defining the ability of textile products to absorb work, could be used in relating fiber and yarn properties to processing efficiency.

It would seem pertinent to point out that some processes might be expected to need strength (not tenacity), while others demand elongation, and others can be postulated to be influenced by average stiffness and/or toughness. For example, perhaps in spinning, strength may be of primary concern, where strength greater than the balloon tension is necessary. In slashing and weaving, a minimum elongation is required. Toughness could conceivably be of importance in spooling and warping and also in sewing. While stiffness is a more difficult property to consider, it would seem to be of significance where a force requirement is first imposed on the yarn, and then without relaxation, a stretch requirement must be met, or vice versa. This might describe the conditions encountered in winding, slashing, or weaving.

Postulating further, for a fiber to spin and a yarn to process properly, minimum strength and elongation values are evidently required; the higher these values, within practical limits, the higher the toughness index and presumably the processability. It is these lower limits that need investigating.

The *variability* and level of break elongation of yarns as well as of strength of yarns should be used as evaluating criteria of processing efficiency, particularly in the case of knitting yarns where yarn elasticity is of paramount importance; and in post-spinning operations, where yarns require a certain minimum "stretch." However, it was found that the value and validity of the use of the variability and level of yarn break elongation as evaluating media of processing efficiency may be significantly influenced by yarn spinning tension, and possibly other spinning and processing variables (worn rings; tape slippage; spindle speeds; incorrect ring, proper flange and traveler combinations, roving twists; etc.).

Yarns are shown to differ in secant modulus which is a measure of their elastic (stiffness) properties. Although no experimental data are available, it is hypothesized that yarns with low modulus or stiffness should withstand processing strains better than yarns of high modulus, all other fiber properties being equal. The usual assumption that a high strength yarn should process more efficiently than a weaker one, using yarn strength as the sole evaluating criterion, may be somewhat misleading. The compensating effects on processing efficiency of the low modulus properties of the weaker yarn may actually neutralize the contributing effects of the high strength yarn to such an extent as to cause both types of yarns to process with equal efficiency.

It is believed that a functional test is needed which will measure the energy capacity of yarns, if the factors contributing to processing are to be more clearly understood—for instance, an impact, or similar energy-measuring test, which measures collectively the tensile and elastic properties of yarns or the use of a toughness index in addition to secant modulus as used in this study.

If subsequent studies show that additional yarn break elongation is needed to attain increased processing efficiency, breeders may have to increase the elastic, as well as some other, properties of the cotton fiber to achieve this objective. Therefore, the use of strength alone may be an insufficient basis for the selection or rejection of experimental cotton varieties.

The recent trend toward development of cottons having unusually high strength may lead to the introduction of varieties from which would be produced yarns having elastic or modulus properties and/or toughness properties detrimental to acceptable operating efficiency. Since such high strength cottons might, for economic reasons, be utilized principally in the finer yarns which normally possess lower break elongation than the coarser yarns, and since spinners generally use high spinning tensions in order to obtain optimum utilization of fiber properties in yarn strength, there is the possibility of approaching a dangerously low level of yarn elasticity which may lead to unpredictable processing difficulties. Breeders should, therefore, recognize these possibilities in planning future breeding programs.

Since cotton fibers differ in elongation and modulus properties, two cottons differing appreciably in these properties may not complement each other in a blend, but instead may produce undesirable results. It is generally well-known that fibers of different elastic properties do not blend compatibly and are undesirable both processingwise and qualitywise. In instances where two types of cottons are known

not to blend satisfactorily, it might be advisable to investigate their elastic properties as the attributable cause of the processing and quality difficulties.

In the course of this work it was desirable to spin 40/1, 60/1, 80/1, and 100/1 yarns in addition to the 15/1 and 30/1 used as bases of this report. Subsequent reports will cover the analysis of data from these remaining yarns.

Acknowledgment

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A Continuous Method of Measuring Yarn Modulus

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THE principle of continuous winding testing of yarn is not new. There is currently offered a machine for continuous yarn testing by Cook and Company of Manchester, England, and one by Goshawk [1] in England. Earlier, in Germany I believe, there was a machine known as the Hahn continuous yarn testing machine, and a number of others have been developed.

In some cases, the device is used only to obtain the number of low level breaks in long lengths of yarn with no means provided for measuring the elongation. The problem is more difficult when accurate measurement of elongation is involved. Frequently, measurement of elongation is replaced by measurement of the force required to produce a fixed elongation.

Though continuous testing may have several advantages over break tests, some of the machines for doing it have been somewhat complex mechanically, and some have had impractical features. In case the yarn is fed in and out of a constant tension loop by means of gripping rolls, the rolls become worn and polished and allow slippage of the yarn in spite of high pressure applied to the rolls. If slippage is recorded as elongation, the result may be subject to large errors.

It is believed that in the machine to be outlined in this paper, the problem of slippage is completely solved by means of snubbing drums. The device is extremely simple, straightforward, and practically free of any type of adjustment. Made of suitable material, it should last indefinitely, requiring no replacement of roll coverings or the like.

A schematic view (Figure 1) shows the yarn being fed over input snubbing drums, forming a loop to support the load, being taken out of the loop by the output snubbing drums, thence to a suitable take-up device. In each pair of drums, one drum is mounted at a slight angle with the other so that the

[1] *J. Textile Inst.* **42**, P8 (1951).

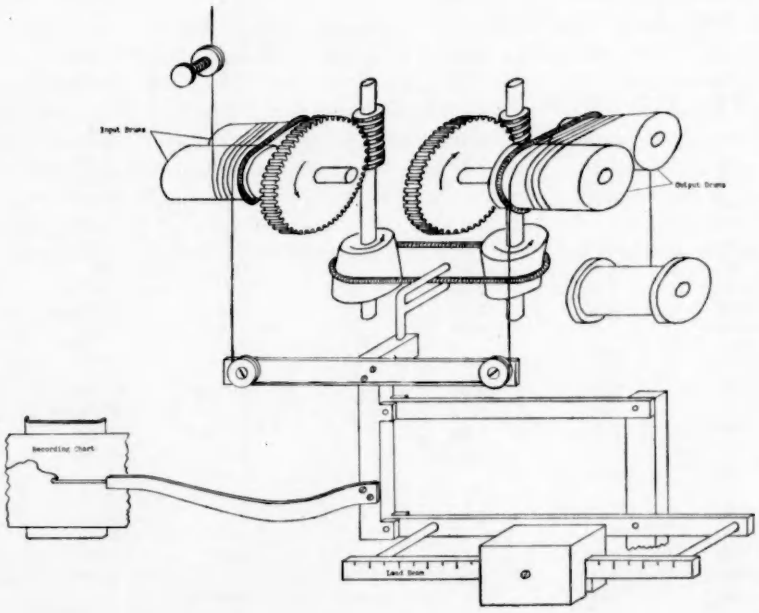

Fig. 1. Continuous winding yarn tester.

yarn advances across the drum faces and does not wind on itself as would be the case with a single drum. Both pairs of snubbing drums are positively driven by worm gears. The worm drives are interconnected by means of a steel belt and cone pulleys. The worm gear driving the input drum is driven at constant speed by a suitable motor. The output worm is driven by the belt from the cone pulley on the power input shaft, and the position of this belt shifts up or down with changes in the elongation of the yarn in the loop. The high gear ratio between the worms and the drum wheels allows the cone pulleys to run at fairly high speed, making it easier to shift the belt rapidly with variation in elongation of the yarn. Also, the high ratio makes the load on the cone belt relatively small which minimizes slippage. Various loads can be applied to the yarn by placing the weight at different positions on the load beam.

By employing the above described snubbing arrangement, many turns of yarn can be used on each pair of drums so that both the input and final take-up tensions may be as small as desired and yet feed the yarn into and take it out of the loop at exactly the speed of the respective drums, with no chance of slippage. The yarn structure is not altered as would be the case if the yarn were fed with squeeze rolls.

A pen arm attached to the assembly transmitting the load to the yarn loop moves up and down with variation in elongation, thereby recording per cent elongation on the chart as the yarn moves continuously through the machine.

TABLE I. Modulus by Continuous Winding Tester Compared with Values by Instron

	Continuous Winding Tester			Instron	
Yarn	Force (g.)	Elongation (%)	Modulus (g./gx/%)	Elongation (%)	Modulus (g./gx/%)
Acetate	25	0.86	0.12	0.20	0.20
(166 gx)	75	2.14	0.095	0.96	0.14
	125	4.72	0.032	2.10	0.045
	150	9.43		5.4	
Cotton	50	1.28	0.15	0.95	0.27
(2-ply)	150	3.20	0.22	2.1	0.26
(350 gx)	250	4.50	0.22	3.2	0.26
	350	5.80		4.3	
Cotton	50	1.28	0.23	0.7	0.27
(Singles)	150	3.85	0.29	2.8	0.32
(175 gx)	250	5.85		4.6	
Rayon	50	0.64	0.30	0.2	0.60
(Filament)	100	1.14	0.17	0.45	0.24
(333 gx)	200	3.86	0.054	1.10	0.075
	300	9.43		5.00	
Dacron	100	0.86	0.86	0.3	1.2
(Filament)	200	1.28	0.83	0.6	1.0
(278 gx)	400	2.14	0.42	1.3	0.55
	600	3.85	0.56	2.6	0.55
	800	5.14	0.56	3.9	0.61
	1000	6.43		5.1	
Nylon	50	5.45	0.44	4.0	0.58
(Filament)	75	7.28	0.31	5.3	0.54
(33 gx)	100	8.57	0.44	6.7	0.47
	125	10.28	0.11	8.3	0.16
	150	14.14		13.0	
Orlon	50	1.50	0.46	0.4	0.75
(Filament)	100	2.80	0.17	1.2	0.22
(83 gx)	150	6.40	0.19	3.9	0.19
	200	9.00	0.28	7.0	0.27
	250	12.00		9.2	

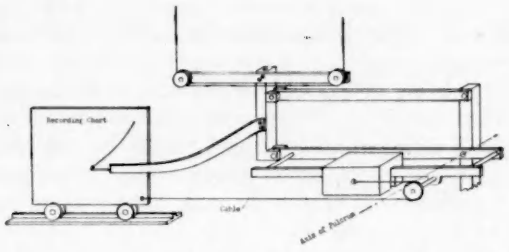

Fig. 2. Arrangement for obtaining stress-strain curve with continuous winding yarn tester.

From the reading of the elongation on the chart and the load setting on the load beam, the average modulus between two given loads can be computed from the following relation:

$$\text{Modulus}_{ab} = \frac{C(F_b - F_a)}{E_b - E_a}$$

where F represents the load, E the elongation, and C a constant depending upon the size of the yarn and the units used. In Table I results taken in this manner for several yarns are shown.

The modulus given by this method of testing yarn is somewhat lower than that obtained from usual stress-strain curves. This happens because as each element of yarn enters the loop it is subjected to the total force for the length of time required to pass through the loop. Applying a given load in this manner will produce greater elongation than when the load is steadily increased from zero upward, allowing each load to exist only for an instant, giving an elongation that is less than would be produced by the same load applied for even a short finite time. This effect was verified on the Instron and Incline machines by placing different fixed loads on the yarn and noting the elongation produced after 10-sec. intervals. It is believed that possibly the constant loading applied to the yarn through a considerable time interval, as is accomplished by this machine, is more like that which yarn will encounter during manufacturing processes, and therefore the modulus computed on results from this machine is possibly more valuable than that computed from conventional stress-strain curves.

It is possible with a modified arrangement to have the machine plot a stress-strain curve, each part of the curve representing the average percentage elongation for any desired length of yarn. The modification required, shown in Figure 2, simply involves having a chart moved horizontally with the weight on the load beam. This makes the horizontal coordinate of the graph represent load, while the vertical motion of the pen gives the percentage elongation. By slowly moving the weight along the load beam from zero load upward, a stress-strain curve is drawn. The oscillations caused by the variations in elongation are superimposed on what would be a smooth curve if the yarn were uniform. To eliminate long range variations in the yarn, the curve can be traced several times for different portions of the yarn. The several tracings will more or less parallel each other, covering an area through which can be drawn an "average" curve. Of course, the machine cannot produce curves extending to the breaking point of the yarn without becoming unthreaded. Figure 3 shows typical curves drawn by the machine.

It is possible to arrange for the weight and chart to be moved back and forth automatically so that the stress-strain characteristics of long lengths of yarn can be displayed without continuous attention of an operator.

If the belt guide is removed, stress-strain curves can be taken with the yarn stationary, by simply moving the weight along the beam, and in this case the load can be increased sufficiently to obtain the

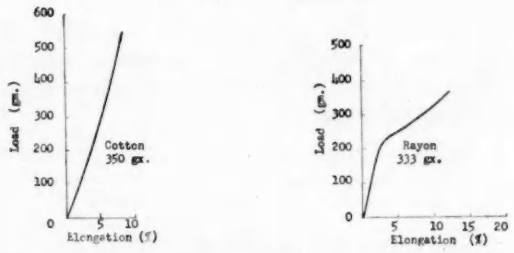

Fig. 3a. Tracings of stress-strain curves drawn by the continuous winding tester.

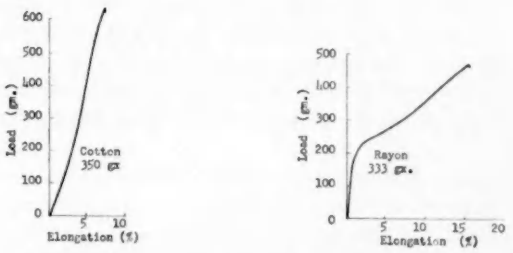

Fig. 3b. Tracings of stress-strain curves drawn by the Instron Tester.

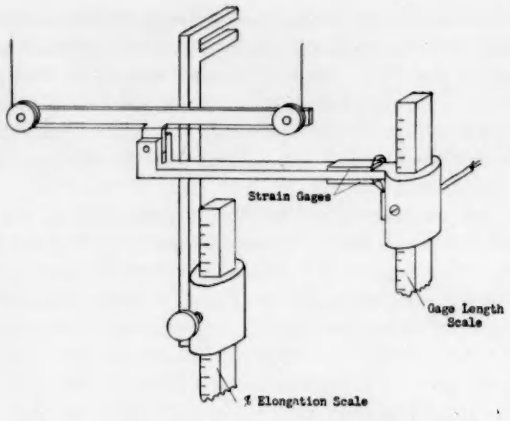

Fig. 4. Arrangement for measuring the force required to produce constant elongation.

breaking strength. Before curves for static tests are made, yarn must be run through at zero tension before each break. By adding suitable jaws, the machine can be used for making standard yarn breaks with definite gauge lengths.

Another application of the machine is to detect and record potential weak places in a yarn. This feature can be accomplished by placing an adjustable "Micro Switch" so that when the elongation exceeds any desired maximum level an electro magnet will lift the load beam before the yarn is entirely broken. By means of a delay mechanism, the load is restored to the yarn after the weak place has had sufficient time to pass through the loop. An electric counter also actuated by the closing of the "Micro Switch" records the number of such weak places in any desired length of yarn.

The machine may be altered to measure force at constant elongation instead of elongation at constant force. To do this the belt guide is arranged to set the percentage elongation to any desired value (see Figure 4). The assembly carrying the loop pulleys is mounted on a strain gauge bar, and the force produced in the yarn is measured by means of a strain gauge amplifier and recorder. The pulley bar may be moved up or down for different gauge lengths. This is probably a better way to operate the machine if an amplifier and recorder are available. In this method, since the belt is not moved by the yarn, there is no delay in readings of the force as is the case when measuring elongation at constant load. Very rapid variations in force can readily be measured by means of the strain gauge set-up. The yarn modulus is computed in the same manner as for the first method of operation.

Advantages of Continuous Yarn Testing

Some of the advantages usually claimed for continuous yarn testing over individual break tests are the following.

1. Since yarn breakage in processing occurs only at the weakest places in a very long length, testing the yarn in such a manner as to measure these very weak places gives a better indication of yarn performance in the mill than conventional single end testing on 10-in. gauge lengths, which gives an average of many strong places and only a very few of the troublesome weak spots.

2. In a given length of time, a much larger amount of yarn can be tested, greatly increasing the chance of finding the weakest places. It is a matter of chance of single thread tests ever finding weak breaks.

3. Yarn can be automatically tested at higher speed than with automatic single thread break testers.

4. Possibly the lower modulus obtained by continuous yarn testing correlates better with ends-down in processing.

The work of comparing this test method with the conventional single end test is to continue. Comparison is to be made of the degree of correlation of each method with such phases of yarn performance as: coefficient of variation in yarn strength, ends-down in spinning, etc.

Acknowledgment

Appreciation is expressed for the suggestions and help in the development of this machine by members of the research staff, Professor J. S. Graham and Machinist Jack Leard.

Trouble Shooting in Textile Processing by Use of the Brush Uniformity Analyzer[1]

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Abstract

There are many mechanical faults in cotton processing which may cause periodic variations in the resulting yarn, roving, or sliver. Each of these defects causes a particular pattern of thick and thin places in the resulting material. An eccentric part (roll or gear) on a drawing, roving, or spinning frame results in a wavy pattern of thick and thin places in the material. The pattern formed in the material by a flat spot in the top roll is dependent upon the position (front, second, third, or back) on the particular frame. A flat spot in the back roll position has very little effect on the resulting material. In the third roll position (four roll frame) it yields a thin place directly followed by a thick spot, while a defective front roll causes periodic thick places in the material.

Defective bottom rolls on the drawing frame affect the sliver differently, depending upon the position on the frame. Defective drafting rolls used primarily as delivery rolls have a greater effect on the resulting material than defective rolls used primarily as feed rolls. Most of these mechanical faults have a particular pattern which can be distinguished by proper use of the Uniformity Analyzer.

There are certain settings (pen average, pen sensitivity, chart speed, and material speed) which can be used on the Brush Uniformity Analyzer to assist in the search for periodic variations. The particular setting to use when searching for periodicities is generally dependent upon the distance between the expected periodic variation. For closely spaced periods (3 to 10 in.) in the material, a fast chart speed (25 mm./sec. or 125 mm./sec.) and the pen average at position 0 or 1 is generally used. A slow chart speed (5 mm./sec.) and the pen average at position 2 or 3 will illustrate longer periodic variations. The pen sensitivity control is generally used to increase the amplitude of the variations on the chart after the pen average and chart speed have been selected.

Introduction

To derive the maximum benefit from an evenness quality control program, means of quickly localizing sources of trouble are needed once it has been established that a process is going out of control. Hit or miss methods of overhauling entire frames are usually unnecessary and needlessly expensive. Frequently, the cause of increases in yarn, roving, or sliver irregularities can be quickly determined by visual analysis of graphic recordings of their weight variations, as this weight per unit length profile may give a rather complete picture of the strand's processing history.

Patterns introduced in each stage of manufacturing are carried through to all subsequent processes, modified by such factors as draft and doubling, and usually swamped over by shorter term patterns from the later stages. For example, the weight profile of a carded cotton yarn is an admixture of short-term patterns from spinning, superimposed on the roving variations, which are now stretched out into longer patterns by the spinning draft; all again superimposed on the weight profile from the drawing operation.

From the simplest possible point of view, if one has a yarn and wishes to obtain some information concerning the weight profile of the roving from which it was made, a basic necessity is a method of filtering out, or cancelling, the variations introduced at the

[1] Taken from a thesis presented in partial fulfillment of the requirements for the M.S. degree in Textile Technology, June 1954, Institute of Textile Technology, Charlottesville, Va.

[2] Present address: Head, Service Records for 13th Infantry Regiment, United States Army, Colorado Springs, Colorado.

spinning frame. In addition, by also filtering out the longer term roving patterns, variations present in the drawing sliver may be more readily seen.

Brush Uniformity Analyzer [3]

The Brush Uniformity Analyzer with recorder chart may be used to depict the weight profile of a strand, including or excluding at will most of the short term variations. Essentially, the Analyzer consists of a measuring head, discriminator, amplifier, and a graph recorder. The strand to be examined is pulled at a specified speed through the measuring head, where variations in mass are reflected as changes in electrical capacity. The discriminator converts these capacity changes to voltage changes, which are amplified and used to drive the recorder, giving a visual record of the weight variations in the material [2].

There are four controls on the Brush Uniformity Analyzer which can be varied to assist in trouble shooting or the search for periodicities, namely, material speed, chart speed, pen sensitivity, and pen average.

The material speeds with which the Analyzer is equipped are 5 ft./sec. and 6 in./sec., although other speeds may be added as a convenience.

Chart speeds in current use are 5, 25, and 125 mm./sec. By varying chart and material speed, it is possible for 1 cm. of chart to represent any of several lengths of strand.

The pen average controls the oscillograph response. It consists of a resistance-capacitance circuit which can be varied to give differing time constants to the signal as received from the discriminator. These different time constants effectively cause different lengths of strand to be "weighed" instantaneously by the Analyzer. The time constants available are 0, 0.1, 0.2 and 0.5 sec., as given by positions 0, 1, 2, and 3 on the control. Where longer time constants are desired, additional capacitors can be added to the circuit. With a material speed of 5 ft./sec., and the control set at position 0, the pen records a continuous weight profile of each $\frac{1}{2}$ in. of material. At position 1, the pen continuously records average weights of each 6 in. of strand, position 2 corresponds to 1-ft. lengths, and position 3 continuously averages over a 30-in. length.

[3] Brush Uniformity Analyzer developed by the Institute of Textile Technology and manufactured by Brush Electronics Company, 3322 Perkins Avenue, Cleveland, Ohio.

In trouble shooting, the pen average control is used to separate the short- and long-term variations. The positions 1, 2, and 3 progressively filter out the short-term variations introduced by the front rolls or front drafting zone to demonstrate the weight patterns due to previous processes.

The pen sensitivity switch controls the amplitude of variations on the chart. With the pen sensitivity set at

Position 1. Normal amplitudes of the weight variations are recorded.

Position 2. Weight variation recordings are twice normal size.

Position Max. Weight variation tracings are approximately four times normal size.

This control is generally used to amplify the variations after determining the proper pen average setting to accentuate periodicities.

Using the Analyzer for Trouble Shooting

To illustrate the use of the Analyzer for distinguishing periodic variations, a yarn was made with 3 periodicities caused by defective front rolls in drawing, roving, and spinning. The regular graph used

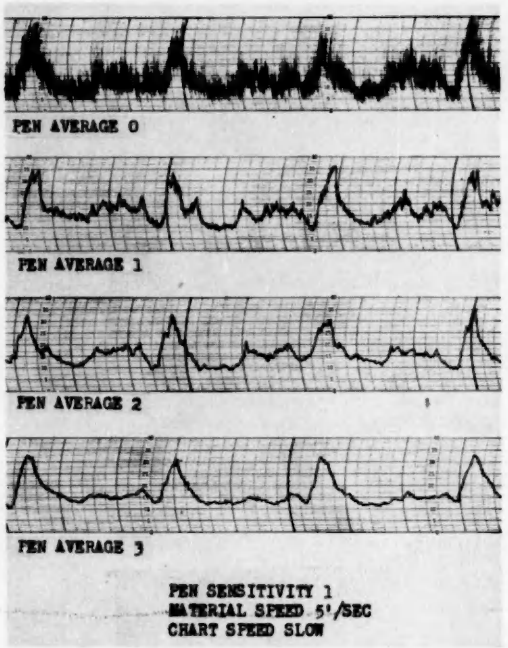

Fig. 1. Graphs of yarn processed with defective front rolls in drawing, roving, and spinning.

for calculating the per cent nonuniformity of the yarn (pen average 0, pen sensitivity 1, material speed 5 ft./sec., and chart speed 5 mm./sec.), is shown in Figure 1. The variation in the yarn due to the defective drawing roll caused the four distinct peaks across the chart. With the pen average at positions 0, 1, and 2, neither the roving nor spinning periodicities were noticeable. With the pen average at position 3, nearly all the variations due to roving and spinning were eliminated, showing only the variation due to the defective roll in drawing.

The pen sensitivity was increased to twice the normal value in the charts shown in Figure 2. With the pen average in position 2, the variation due to the eccentric top roll in roving was visible along with the variation due to the drawing defect. This was the only setting at which the periodic variations in roving could be easily distinguished.

For a close analysis of the exact pattern of the periodic irregularity caused in spinning, the pen sensitivity was increased to position 2 and the chart speed increased to 125 mm./sec. The type of chart obtained with these settings is shown in Figure 3.

Calculation of Wave Lengths of Periodic Variations

The calculation of the length of a periodicity due to a mechanical fault in the spinning, roving, or drawing operation is simple.

A periodicity due to roll defects (eccentricity, flat spots, soft spots, bent rolls) is equal in length to the roll circumference times the draft. For example, a period due to an eccentric third roll in drawing is determined as follows:

Diameter of roll 1.25 in., Draft from third roll 4.4, Roving draft 10, spinning draft 20.

Period in drawing sliver $= 1.25 \times \pi \times 4.4 = 17.27$ in.

Period in roving $= 17.27 \times 10 = 172.7$ in.

Period in yarn $= 172.7 \times 20 = 3454$ in.

One of the simpler methods of determining the period length due to a gear fault is to determine the (in./min. delivered)/(r.p.m. of the gear). This gives the length in inches of an expected periodicity due to a gear defect.

Determining the defect pattern which occurs only when a traverse passes a certain critical point is

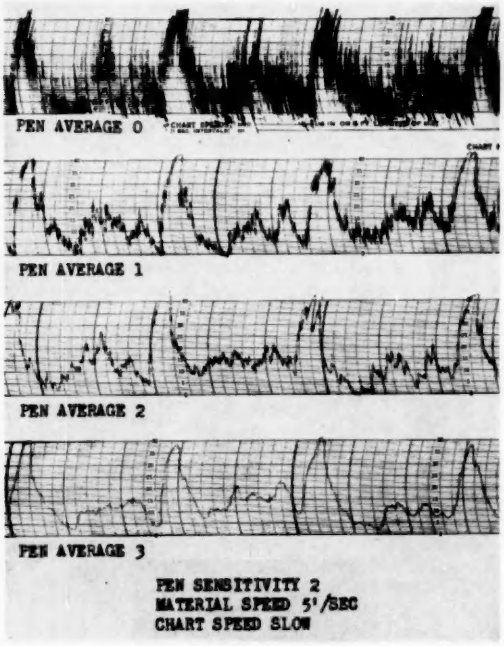

Fig. 2. Same yarn as in Fig. 1, with increased sensitivity, to show period due to defective roll in roving.

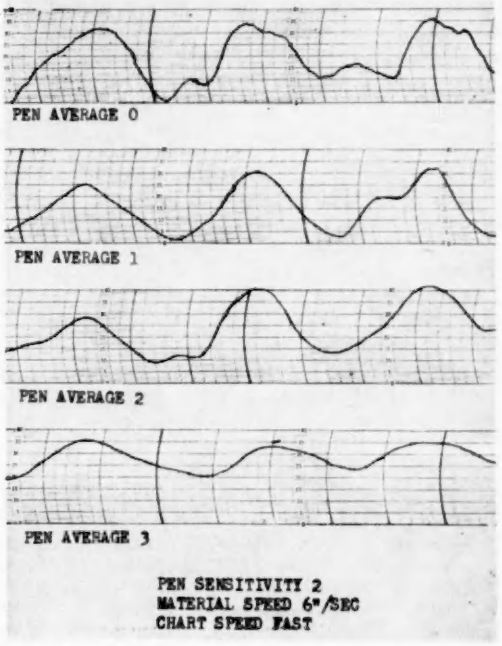

Fig. 3. Same yarn as in Fig. 1, with decreased yarn speed, increased chart speed, to show period due to defective roll in spinning.

complicated by the different distances between the apparent defects. There are three distinct possibilities.

1. A fault at the extreme end of the traverse would make the space between irregular places equal to the length of product delivered per cycle of traverse.

2. A defect directly in the center of the traverse would give a period equal in length to half the length delivered per cycle of traverse.

3. A fault at any intermediate point would result in two irregularities at different distances. There would be two closely spaced periods, separated periodically by longer spaces, all proportional to the distance from the defect to the end of the traverse.

A number of mechanical defects were introduced in processing and the Uniformity Analyzer settings determined for best depicting these defects. These findings, arranged according to the material tested and the defective process, are shown in Table I.

Defects Reproduced in Processing

Sliver Defects

Mechanical faults in drafting which cause periodic variations include drafting roll defects and gear defects. To demonstrate the patterns introduced in the resultant product, the following defects were induced at the drawing frame.

1. Chip of metal between the flutes of the bottom rolls.

2. Eccentric top drafting rolls (0.06 in. eccentric).

3. Flat spot in top rolls (0.03 in. shaved off).

4. Eccentric gear at the end of the third drafting roll (0.03 in. eccentric).

A periodic defect due to a chip caught in a flute of the back bottom roll on the drawing frame is illustrated in Figure 4. The resulting period was equal to

Roll circumference × Total draft *

$1\frac{3}{8}$ in. × 3.14 × 5.55 = 24 in. = 2 ft.

In the roving, the period length is

Period in the sliver × roving draft

2 ft. × 11 = 22 ft.

And in the yarn,

Period in roving × yarn draft

22 ft. × 20.6 = 453 ft.

These periods are all apparent in all graphs. However, it may be noticed that the peaks are accentuated by use of increased sensitivity and pen averaging.

A chip in the third bottom roll of the drawing frame resulted in a sliver periodicity of 15.2 in., as shown in Figure 5. Notice how this pattern differs

* For this first defect, calculations of expected period length are shown. In all subsequent examples, the length only is given, with the method of calculation being similar to the above.

TABLE I. Recommended Settings to Determine Periodic Variations

Defect				Analyzer settings			
Material tested	Defective part	Position	Frame	Material speed/sec.	Chart speed (mm./sec.)	Pen average position	Pen sensitivity position
Yarn	Roll	Front roll	Spinning	6″	25	0 or 1	2
				5′	125	0	1
Yarn	Roll	Back roll	Spinning	5′	25	2 or 3	2
Yarn	Groove in top roll	Back roll	Spinning	5′	5	2 or 3	2
Yarn	Roll	Front	Roving	5′	5	2 or 3	2
Yarn	All roll defects prior to front roll in roving			5′	5	3	3
Roving	Roll	Front	Roving	6″	25	0 or 1	2 or 3
Roving	Roll	Second	Roving	6″	5	2 or 3	3
Roving	Roll	Third	Roving	6″	5	3	3
Roving	Roll	Back	Roving	6″	5	3	3
Roving	Roll vibration		Roving	6″	25	0	3
Roving	All drawing defects	Any	Drawing	6″	5	3	3
Sliver	Roll	Front	Drawing	6″	25	0	3
Sliver	Roll	Second	Drawing	6″	5 or 25	3	3
Sliver	Roll	Third	Drawing	6″	5	3	3
Sliver	Roll	Back	Drawing	6″	5	3	3
Sliver	Gear	Third roll	Drawing	6″	5	3	3

from Figure 4, which shows periodic thick spots between which the pattern is normal. In this case, the chip causes the third top roll to rise momentarily from the bottom roll, causing an increased draft at the nip of the second roll. At the same time, the back rolls continue delivering sliver to the third rolls and a thick spot results, since these rolls are not drafting at this instant. For these reasons, both thick and thin periodic changes are noted.

In roving the fault is not noticeable at normal %NU settings, but is readily detectable with the pen average at position 3 and the pen sensitivity at a maximum setting. The period in the roving is 14 ft. The yarn graph at regular settings was not satisfactory to characterize the defect; however, the use of increased averaging and sensitivity again shows the period quite distinctly. A chip in the flute of the front roll gives a pattern, as shown in Figure 1.

Eccentricity in the top rolls causes the nip of the roll to move backward and forward, periodically increasing and decreasing the draft between the rolls. The resultant thick and thin places for a front roll defect were readily distinguished in sliver and yarn at any settings, but the contrast was greater at the settings indicated. The regular %NU graph of the roving failed to show this defect, but at pen average 3 and maximum pen sensitivity, the period is distinct (Figure 6). The pattern formed by eccentric rolls is symmetric, with the distance between thick spots equal to the distance between thin spots.

Eccentric second, third, and back rolls were discernible only with the special settings. This is because the thick and thin spots in the strand are attenuated by the increased total draft, and obscured by the short-term irregularities present. The use of higher pen averaging filters out these short-term unevennesses, and exposes the longer periods for observation.

Patterns produced by a flat spot in the top roll are dependent on the position in which the roll is placed; i.e., front, second, third, or back. In the front roll position there was a sharp, short thick spot followed by a longer thin place (Figure 7). The thick spot

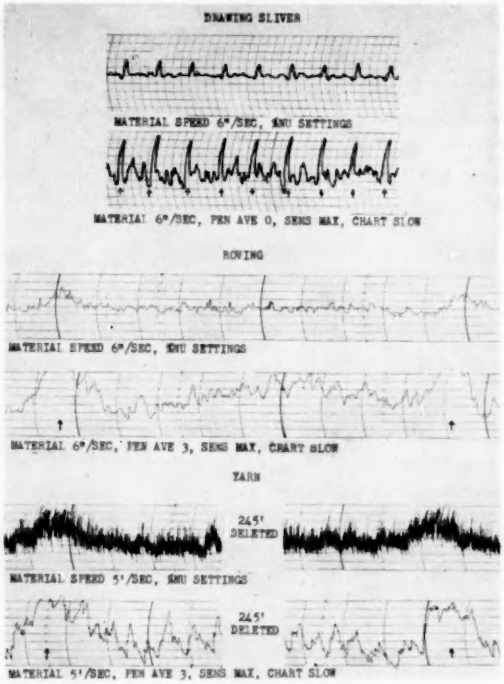
DRAWING SLIVER
MATERIAL SPEED 6"/SEC, %NU SETTINGS
MATERIAL 6"/SEC, PEN AVE 0, SENS MAX, CHART SLOW
ROVING
MATERIAL SPEED 6"/SEC, %NU SETTINGS
MATERIAL 6"/SEC, PEN AVE 3, SENS MAX, CHART SLOW
YARN
245' DELETED
MATERIAL SPEED 5'/SEC, %NU SETTINGS
245' DELETED
MATERIAL 5'/SEC, PEN AVE 3, SENS MAX, CHART SLOW

Fig. 4. Metal chip in a flute of back bottom drawing frame roller; period length 24, 264, and 5450 in. for sliver, roving, and yarn.

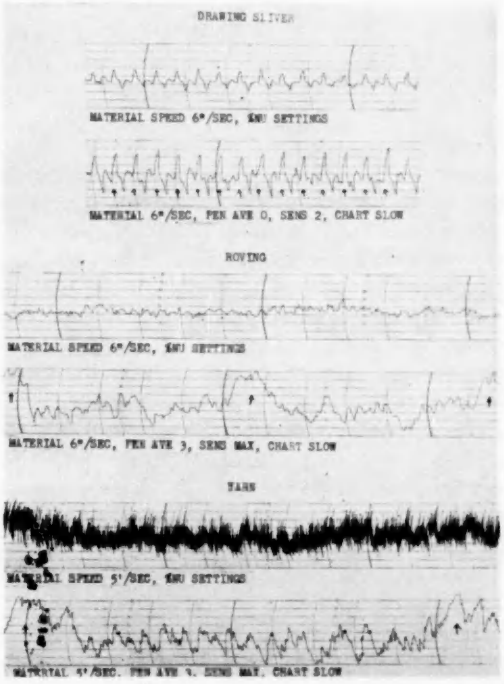
DRAWING SLIVER
MATERIAL SPEED 6"/SEC, %NU SETTINGS
MATERIAL 6"/SEC, PEN AVE 0, SENS 2, CHART SLOW
ROVING
MATERIAL SPEED 6"/SEC, %NU SETTINGS
MATERIAL 6"/SEC, PEN AVE 3, SENS MAX, CHART SLOW
YARN

Fig. 5. Metal chip in a flute of third bottom drawing frame roller; period length 15, 167, and 3420 in. for sliver, roving, and yarn.

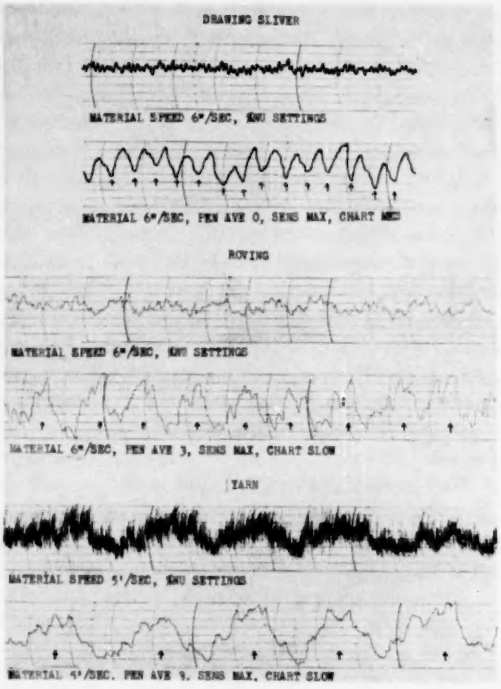
DRAWING SLIVER
MATERIAL SPEED 6"/SEC, SNU SETTINGS
MATERIAL 6"/SEC, PEN AVE 0, SENS MAX, CHART MED
ROVING
MATERIAL SPEED 6"/SEC, SNU SETTINGS
MATERIAL 6"/SEC, PEN AVE 3, SENS MAX, CHART SLOW
YARN
MATERIAL SPEED 5'/SEC, SNU SETTINGS

Fig. 6. Eccentric front top drawing frame roller; period length 3.14, 34.6, and 713 in. for sliver, roving, and yarn.

was probably caused when the front top roll stopped momentarily, due to slippage at the flat spot, and the second rolls continued to feed cotton to the front rolls; then as the front roll started again, the thick spot was drawn through the front rolls. Since the calender rolls continued to revolve at the time the front roll was momentarily stopped, a thin spot was formed by the drafting action. The periodicity in yarn, roving, and sliver is best seen at the special Analyzer settings.

The patterns formed by a flat spot in the second and third top rolls are similar to those shown in Figure 7, except the flat spot in the third top roll causes a more pronounced thin place than thick. The thick spot is not as prominent because the back roll was rotating so slowly that no appreciable amount of stock was delivered.

To demonstrate the effect of a defective gear, an eccentric gear was placed at the end of the third bottom drafting roll, and the roll bearings near the gear loosened to allow the roll to move freely. As the gear revolved, a to-and-fro motion similar to an eccentric roll was induced. The type pattern caused by this condition is similar to Figure 6.

Roving Defects

Periodic variations were reproduced in roving due to

1. Flat spot in top drafting rolls (0.03 in. shaved off)
2. Eccentric top rolls (0.06 in. eccentric)
3. Vibrating roll.

The type of periodicity caused by a flat spot in the third top roll in roving is shown in Figure 8. This pattern was not detectable at regular settings but was readily seen at the special settings indicated in both roving and yarn.

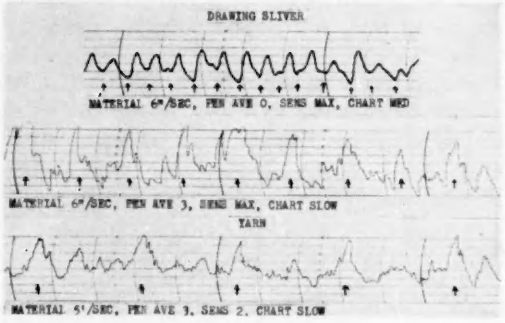
DRAWING SLIVER
MATERIAL 6"/SEC, PEN AVE 0, SENS MAX, CHART MED
MATERIAL 6"/SEC, PEN AVE 3, SENS MAX, CHART SLOW
YARN
MATERIAL 5'/SEC, PEN AVE 3, SENS 2, CHART SLOW

Fig. 7. Flat spot in front top drawing frame roller; period length 3.14, 34.6, and 715 in. in sliver, roving, and yarn.

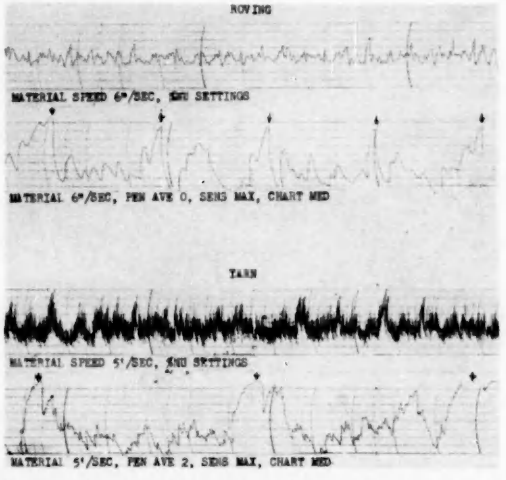
ROVING
MATERIAL SPEED 6"/SEC, SNU SETTINGS
MATERIAL 6"/SEC, PEN AVE 0, SENS MAX, CHART MED
YARN
MATERIAL SPEED 5'/SEC, SNU SETTINGS
MATERIAL 5'/SEC, PEN AVE 2, SENS MAX, CHART MED

Fig. 8. Flat spot in third top roll on roving frame; period length 14 in. for roving and 289 in. for yarn.

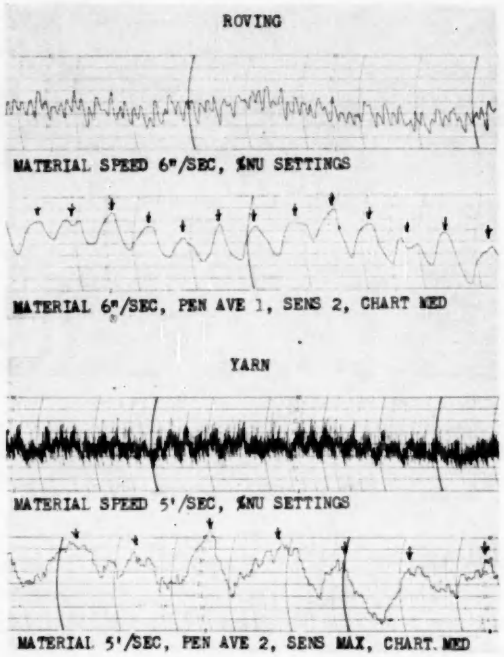
ROVING
MATERIAL SPEED 6"/SEC, %NU SETTINGS
MATERIAL 6"/SEC, PEN AVE 1, SENS 2, CHART MED
YARN
MATERIAL SPEED 5'/SEC, %NU SETTINGS
MATERIAL 5'/SEC, PEN AVE 2, SENS MAX, CHART MED

Fig. 9. Eccentric front top roll on roving frame; period length 3.74 in. for roving and 77 in. for yarn.

Defects due to flat spots in other top rolls also are not visible at regular settings, but may be seen at special settings. The type of pattern is again dependent on which roll is defective.

Addition of eccentric top rolls to the roving frame produced patterns, as shown in Figure 9. The patterns were not discernible at regular per cent nonuniformity settings; however, at increased pen average and sensitivity all the periods were readily seen. The mechanism of period formation due to eccentric rolls is discussed in the section on drawing frames.

Spinning Defects

The following defects were reproduced in spinning to illustrate some of the possible faults in top rolls used on the spinning frame.

1. Soft spot in roll (made by placing in acetylene tetrachloride).
2. Flat spot in roll (0.015 in. shaved off).
3. Eccentric top rolls (0.03 in. eccentric).
4. Groove in back top roll.

A soft spot in the front top roll caused a period in the yarn 3.64 in. long ($1\frac{5}{32}$ in. $\times$ 3.14). This period was not seen at normal per cent nonuniformity settings but was readily apparent at increased chart speeds (Figure 10). A soft spot in the second top roll showed no apparent periodicity in the yarn.

An extreme increase in yarn irregularity resulted from using a front roll with a flat spot present. However, no periods could be seen at the regular settings. Use of an increased chart speed (Figure 11) showed this period of 3.64 in. Periods due to eccentric top rolls also were not visible at regular settings, but again were easily seen at special settings.

A narrow groove was formed in the top back roll. As the traverse motion passed this point, the roving was pulled through in clumps by the second drafting roll, causing a thick place in the resulting yarn. The groove was placed one-fourth of the distance from one end of the traverse. This effectively caused two periods in the yarn, at lengths of 155 and 454 in., Figure 12.

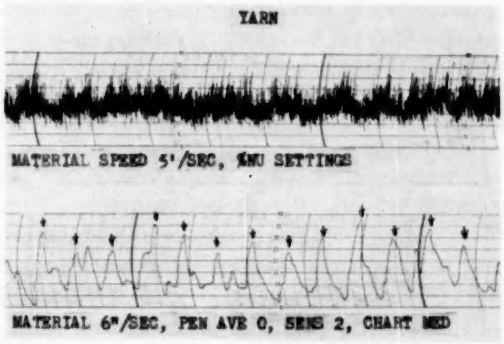

Fig. 10. Soft spot in front top roll on spinning frame; period length 3.64 in. in yarn.

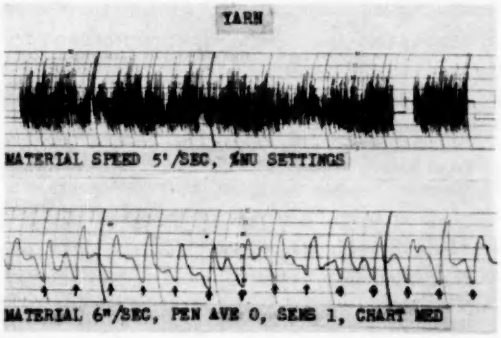

Fig. 11. Flat spot in front top roll on spinning frame; period length 3.64 in. in yarn.

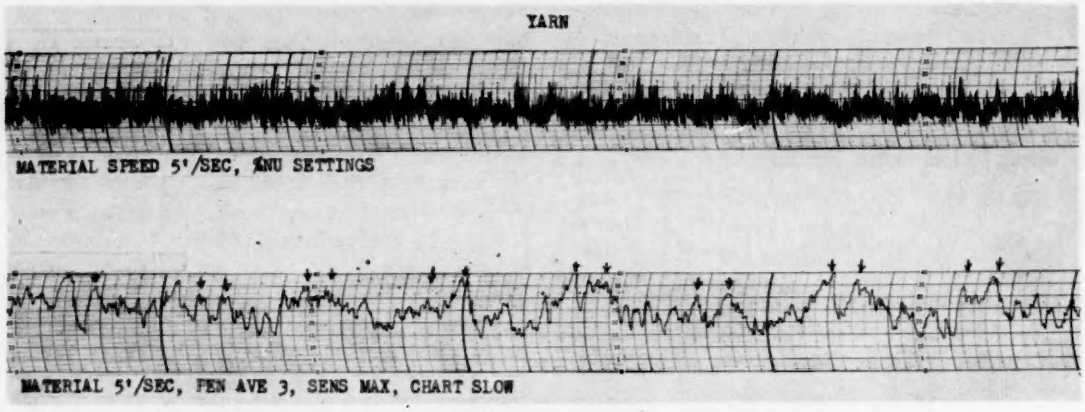

Fig. 12. Grooved back top roll on spinning frame; period lengths 154.5 and 453.5 in. in yarn.

Limitations

These data are intended only as a guide toward a trouble shooting program. Many points in processing which might cause periodicities have not been investigated as yet, such as bent shafts, gear defects, apron drafting zones, etc. In addition, defects in processing seldom cause precise periods in the product due to the effects of roll slippage, play in gears, and other factors.

Excessive variations of a nonperiodic nature may frequently obscure some periodic patterns, and the presence of two conflicting periods in a strand may make visual analysis impossible. In cases such as these, more elaborate methods of depicting periodicities are needed.

Settings to Determine Periodic Variations

Periodic variations in yarn, roving, and sliver due to mechanical faults were reproduced in drawing, roving, and spinning. Each of the defective materials was tested on the Brush Uniformity Analyzer and the combination of pen average, pen sensitivity, chart speed, and material speed determined which best illustrates the periodic variations in the material on the uniformity charts. These settings are summarized in Table I.

Conclusions

1. Many periodic variations which normally could not be detected at the regular per cent nonuniformity

TABLE II. Draft Distribution and Roll Diameter Information for Defects Introduced in Processing

Drawing Defects		Roving Defects		Spinning Defects	
	Roll diameter (in.)		Roll diameter (in.)		
Back bottom	1 3/8	Back bottom	1	Top roll diameter	1 5/32 in.
Third bottom	1 3/8	Third bottom	1	Total draft	30
Second bottom	1 1/8	Second bottom	1	Inches of yarn delivered	
Front bottom	1 1/4	Front bottom	1 1/8	per cycle of back roll	
Top rolls	1	Top rolls	1 3/16	traverse	618
	Draft distribution		Draft distribution		
Back to third	1.6	Back to third	3.08		
Third to second	1.2	Third to second	1.05		
Second to front	2.85	Second to front	3.57		
Total	5.55	Total	11.5		
Roving draft	11	Spinning draft	20.6		
Spinning draft	20.6				

settings can be distinguished with the Brush Uniformity Analyzer with other settings.

2. The particular settings to use are generally dependent upon the length of the expected periodic variation. For example, for closely spaced periods, a fast chart speed with little averaging gives the best results. For longer spaced periods, a slow chart speed with greater filtering (higher positions on pen average control) would be used.

3. Periodic variations may frequently be obscured by excessive nonperiodic variations or other conflicting periods.

4. In some cases periods caused by a defect in one process may not be distinguished in the material from that process but become evident in subsequent processing.

5. Particular faults in a process frequently have different patterns of thick and thin places depending on the position on the frame (front versus second rolls, etc.).

Acknowledgment

Appreciation is expressed to Dr. Jack Compton, Technical Director, and to the Board of Trustees and Technical Advisory Committee of the Institute for permission to publish the findings of this study.

Literature Cited

1. The British Cotton Industry Research Association, *A Guide to the Use of Regularity Testers in Spinning Mills*, Pamphlet No. 61 (October 1953).
2. Institute of Textile Technology, *Confidential Research Report No. 25* (June 1950).

Book Reviews

Some Aspects of the Crystallization of High Polymers. G. Schuur. Communication No. 276. Delft, The Netherlands, Rubber-Stichting, 1955. 82 pages. Price, 5 Dutch florins.

Review by Robert A. Florentine, Research and Development Division, American Viscose Corporation, Marcus Hook, Pa.

The author attempts to interpret structural properties of high polymers on the basis of possible formation of spherulites, small ordered regions, close packed and discontinuous, which are apparent in some polymers (guttapercha, rubber hydrochloride, polyethylene) when observed under polarized light. These spherulites are considered to be the result of an internal flow of material just prior to crystallization.

From a study of stress-strain relationships of variously stretched samples of rubber hydrochloride monofilaments, there is advanced a theory of "continuous crystal lattice" which is proposed to exist simultaneously with a "continuous amorphous region." "The high elastic elongation of oriented rubber fibers is not caused by the 'amorphous regions,' but is a direct result of macromolecular character, which causes a backward slip of the crystal plane."

The rate of crystallization and the melting of high polymers are also considered and are found to be complex. The length and flexibility of the macromolecules prevent the attainment of equilibrium and make a thermodynamic analysis difficult, if not impossible. Spherulite formation is sometimes anomalous, but qualitative relations have been found between spherulite size and rate of crystallization in very dilute solutions.

The application of the author's ideas of crystallization to fiber theory and technology may be difficult. The simultaneous continuity of the amorphous and crystalline phase is an arresting concept for students of fiber structure.

The proposal of crystal-plane slip with stretching may not find widespread acceptance in the fiber field. The elastic characteristics studied are in a range of ten times that of textile fibers; data in the lower region may demand judicious interpretation. In the author's words, " . . . the crystallization and melting of high polymers is very complicated . . . " and it remains so.

The text includes 35 photographs and figures, and 101 references, containing most of the literature on spherulites in high polymers to October, 1954.

The Structural Chemistry of Proteins. H. D. Springall, New York, Academic Press, Inc., 1954. x + 376 pages. Price $6.80.

Reviewed by Joseph H. Dusenbury, Textile Research Institute, Princeton, N. J.

This is a splendid book. In it Professor Springall has collected and summarized in impressive fashion the many kinds of experimental information that have been used to give us our present knowledge of the structure of proteins. The broadest kind of interpretation has apparently been applied to the words, "structural chemistry," for the book scans a wide spectrum of researches ranging from classical organic to theoretical physical chemistry. In his Preface, Professor Springall explains that this volume has evolved from a course of lectures given to senior undergraduate and graduate students at the University of Manchester. If the quality of those lectures is reflected in this work, the students involved at Manchester were uncommonly fortunate.

The first two chapters (Introduction, Peptide Syntheses) deal with the chemical evidence for the polypeptide structure of proteins and discuss the organic-chemical procedures used to form polymers of α-amino carboxylic acids. The next chapter discusses fibrous proteins and makes use of the two-group classification system of Astbury: the *k.m.f.*-group (keratin-myosin-fibrinogen) and the collagen group. The important contributions of X-ray diffraction, infrared spectroscopy, and electron microscopy to solving the fibrous protein problem are described and correlated. The evidence for the zig-zag form of the polypeptide chains in the stretched β-state of *k.m.f.*-group fibers is critically discussed, and there is a masterful summary of the work, principally of Pauling and Corey, that indicated a helical configuration as the best model for the form of the polypeptide chains in the unstretched α-state of the *k.m.f.*-group proteins and collagen. The author points out in a footnote that it is unfortunate this chapter went to press too early to include the 1952 Royal Society discussions on protein structure. This reviewer feels, however, that such an omission is of minor importance in this case. The fourth chapter (Globular Proteins) discusses the characteristics of soluble proteins and the methods used to measure their sizes, shapes, and molecular weights. Here measurements of osmotic pressure, diffusion and sedimentation constants, viscosity, and light-scattering characteristics are considered, and the reader is cautioned to take some of the conclusions based on these measurements with an appropriate number of grains of salt. The fifth, final, and longest chapter in the book is about the analytical chemistry of proteins and amino acids. If the reviewer were called upon to pick a favorite chapter, this would be it. The discussion of the chemical methods used to learn of the amino-acid composition of proteins and of the sequence of amino acids along a polypeptide chain is beautifully done. The descriptions of how amino acids are separated and identified by chromatographic techniques are particularly good.

In terms of the 1954 publication date, the bibliographies (one for each chapter) appear to be complete, and they are quite extensive. There are author and subject indices and an index of "named" proteins and natural peptides. The subject index is well-planned and, happily, contains only three page references under "Proteins." The 115 figures and 23 tables in the book are instructive and contribute to its attractive format.

In the Foreword to the book, Professor Linus Pauling comments favorably upon the author and the results of his work and concludes with the sentence: "I expect that the book will be found valuable not only to chemists and biologists who are working with proteins, but also to others who have an interest in the subject." In the opinion of at least one reader, this is understatement.